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A Thesis Entitled

AN INVESTIGATION OF SOME SOURCES OF ERROR IN APPLIED  
GEOCHEMICAL DATA FROM SOUTH DEVON, ENGLAND.

Submitted for the Degree  
of Doctor of Philosophy  
in the  
Faculty of Science, University of Leicester  
by

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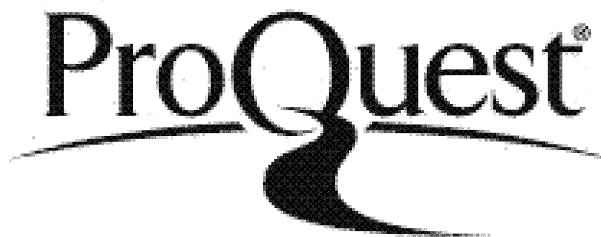
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## ABSTRACT

An investigation of some sources of error in applied geochemical data from South Devon, England. By: Nigel William Radford

Various aspects of analysis by AAS have been investigated. Digestion of 0.5g of minus 125 micron material in 4M  $\text{HNO}_3$  at 95°C for 4 hours seems to be the optimum for such elements as Cu, Pb, Zn, Fe and Mn. Tin determination by AAS, using an air-acetylene flame, is possible, but problems with the ammonium iodide digestion used, remain to be solved. However, the selection of minus 190 micron material as optimum for Sn may be of only local significance.

Some interference effect was observed when different weights of the same samples were analysed, and a spectral interference between Cu and Ag has been detected under certain conditions. Some losses of reproducibility result from evaporation from aqueous digestions after storage for only a few hours in unsealed containers. The postulated presence, in stream sediments, of  $\text{HNO}_3$ -soluble ferric arsenate, and the above digestion, permit As determination by conventional AAS.

Standardised, systematic techniques for such processes as drying and sieving of samples are shown to be necessary in order to achieve good reproducibility.

Partition of error variance has demonstrated that, unless analytical detection limits are approached, sampling error dominates sub-sampling and analytical errors. Various aspects of sampling error have been investigated.

The lowering of AAS detection limits, by the use of flame-less atomisation techniques, means that a case may now be made for the use of acidified natural water samples as a regional as well as follow-up, sampling medium. The dependence of metal partition between sediment and water on physico-chemical properties of the stream has been demonstrated. Therefore, a complete understanding of secondary dispersion can only be achieved if water, as well as sediment, is analysed.

Significant seasonal variations in metal content of both sediment and water samples have been detected and related to the groundwater/surface run-off system.

The data from the main field area, at Yarner Wood, has been evaluated in the context of the mineralisation believed to be present.

A Thesis Submitted

IN FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF

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SCHOOL OF DISTANCE EDUCATION

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## CHAPTER 1

### INTRODUCTION

#### 1.1 VARIANCE IN APPLIED GEOCHEMICAL DATA

#### 1.2 OBJECTIVES OF THE PRESENT STUDY

#### 1.3 AREAS CHOSEN FOR SAMPLE COLLECTION

#### 1.4 SOME DEFINITIONS AND STATISTICS

#### 1.5 ACKNOWLEDGEMENTS

## CHAPTER 1

### INTRODUCTION

#### 1.1. VARIANCE IN APPLIED GEOCHEMICAL DATA

The drainage channel represents a clearly defined environment into which are concentrated the products of secondary geochemical dispersion (e.g. see Hawkes and Webb (1962), Chapter 7, for a description of secondary dispersion processes). Attempts to evaluate the bedrock geochemistry of a given area, for whatever purpose, may be made via drainage channel material, since it may be assumed that all bedrock units upstream of a given point, will contribute geochemically, to a greater or lesser extent, to the drainage channel material (sediment and/or water) at that point.

Techniques involving the chemical analysis of material from drainage channels were mostly developed in attempts to detect mineralised ground (i.e. metal rich bedrock units). The initial, post-war success of stream sediment geochemistry, as an exploration tool, was based largely upon the detection of so-called "sore-thumb" anomalies. Baldock (1977, Fig. 3) gives an example of such an anomaly detected during a recent study in Peru. Even poorly designed and executed geochemical surveys (sometimes dubbed "bucket-geochemistry"!) ought to detect such large-contrast anomalies, but as such anomalies are detected, fewer remain to be found. If more subtle geochemical anomalies are to be detected, and indeed if the results of geochemical mapping for whatever purpose, are to be interpreted with confidence (see e.g. Webb et al. (1968)), then the sources of error, to which this type of work is prone, must be better understood, and, as far as possible, eliminated.

Some concepts of error in applied geochemistry were developed by Miesch (1967 and 1971), and enlarged upon, with specific reference to the drainage channel environment, by Howarth and Lowenstein (1971).

A detailed review of these theories was given recently by Duff (1975 , Chapter 2) and unnecessary duplication of his work will result from any lengthy attempt to further elaborate upon them. However, some brief definition of the present author's interpretation of certain terms and concepts related to error, may be useful at this point.

As previously mentioned, the drainage channel concentrates the secondary dispersion products from all bedrock types in the catchment area. The exact proportions in which each bedrock type contributes to the stream load at any one point, is a matter of natural selection. This natural or regional variability is the desirable feature of a drainage channel survey, and the interpretation of such variations is the aim of the applied geochemist.

The distribution patterns caused by such natural variability, however, may become distorted since the techniques involved in a drainage channel survey can contribute errors of various types. The sampler cannot collect all the material available at any sample locality, and so a small, hopefully representative amount is selected. The parameters upon which this selection are based may be sound (i.e. an attempt may be made to fill the sample bag with small quantities of sediment from many different individual spots in the stream) or they may be trivial (e.g. the depth of the water in relation to the sampler's boots, the ease with which he may hop from boulder to boulder etc.). Under any circumstances, it will be fortuitous if the sample collected is truly representative of the entire bed load at that particular point, and highly unlikely that the same good fortune will apply to other samples. Thus, to the natural variability of the material has now been added an extra factor, sampling variability.

Further selections, in the laboratory, influence the reproducibility of the final data. For example, sub-sampling variability will be introduced by the fact that, in a practical situation, only a small portion of the field sample can be analysed. Thus some form of screening and splitting of the sample (if it is a solid sample) must take place prior to analysis. No analytical technique can be expected to be completely reproducible, and therefore further error is likely to be introduced, here referred to as analytical variability.

Thus, the overall data variability is compounded from the natural variability, plus sampling, sub-sampling and analytical variability. These latter three are commonly lumped together, and referred to as the total error variability. It is, thence, but a small step to deduce that increasingly subtle patterns in natural variability will only be detected if the error sources of variability can be reduced.

## 1.2 OBJECTIVES OF THE PRESENT STUDY

Broadly speaking the objectives of the present study are:-

- (a) to evaluate the extent to which the various sources of error contribute to overall variability in geochemical data, and:-
- (b) to modify the criteria used for making selections at various stages in the process, and thereby to attempt to reduce these sources of error, thus increasing the degree of confidence with which the geochemist may interpret any natural variability displayed by his results.

A pre-requisite of any such investigation is that analytical errors be minimised, or at least that the analytical process be optimised, which involves striking balances between numerous factors.

It will be demonstrated that fine-grained material is preferable when analysing for most of the elements of concern in this study. Therefore, a balance must be struck between, on the one hand, collecting logistically convenient sized samples in the field and, on the other, having plenty of very fine-grained material available for analysis. Furthermore, in order to overcome sub-sampling error (the theory of which is dealt with at length by Duff (op. cit., section 2.4)), very large sub-samples are required. However, one of the principal attractions of applied geochemistry in mineral exploration, is that it is capable of dealing with large numbers of samples very quickly. To develop techniques, however reproducible they may be, which necessitate the use of large sample containers rather than test tubes for sample digestion, would detract seriously from the speed factor in applied geochemistry. The use of very large sample weights may also slow down such processes as sieving, and weighing out of sub-samples. Thus, an optimum process for most of the elements of interest in this study, involves the use of the most reproducible analytical method available, in conjunction with suitable sample digestion techniques, operating on a conveniently sized quantity of as fine-grained material as possible, within the practical limits set by sample collection. Data will be presented to support the use of AAS for analysis for copper, lead, zinc, iron and manganese, following a four-hour digestion in 4M  $\text{HNO}_3$  at 95°C of 0.5g portions of minus 125 micron material.

Confident that his analytical technique contributes in only a minor way to overall variability, the geochemist may assess the other forms of error variability by means of replicate sample collection. The

theory of partition of error variance will be developed, and a detailed field investigation used to demonstrate that in the area sampled, sampling is the dominant form of error variance, in stream sediments, for eight of the nine elements considered. Some causes of sampling error will be discussed in the light of this conclusion. Comparisons with a previous, detailed study of the same region (Harrison, 1974) will be used to demonstrate the effects on error variability of the modified techniques adopted during the present study.

Various aspects of sample preparation technique will be discussed and it will be demonstrated that loss of reproducibility can be expected unless rigorously standardised techniques are adopted for such processes as sample drying, sieving, splitting and sub-sampling.

Detailed investigations will be presented which deal with analytical errors, especially associated with AAS analysis, but also associated with colorimetric determinations of tin. Instrumental, or re-reading errors, and changes in strength of standard solutions, contribute to direct variability in the analytical process. Other sources of variability, related to changes in technique, have also been investigated. Serious loss of reproducibility may result from evaporation of liquid sample material during storage prior to analysis. Substantial variations in reported metal concentration were observed in different-sized samples of the same material, and detailed investigation of the phenomenon implies that it may be caused by some form of matrix interference in the AAS process, but a complete understanding of it will require further work. A similar problem related to tin analysis was attributed to inefficiencies in the digestion technique. Data will be presented to support the use of nitric acid as a medium for digesting samples, prior to AAS analysis for arsenic, provided that the arsenic is present in the form of ferric arsenate. Data will also be presented which indicates some degree of spectral interference, during

AAS analysis, for copper and/or silver, under certain conditions.

In view of the dominant role played by sampling error during sediment collection, an investigation of water as a sampling medium was undertaken. Data will be presented to support the view that water is a relatively homogeneous sampling medium and that AAS analytical techniques, especially when flame-less atomisation is available, are capable of detecting significant metal distribution patterns in suitable natural water samples. Furthermore, it will be demonstrated that the drainage channel environment is a two-phase system in which chemical and physico-chemical equilibria are present between sediment and water. This makes analysis of water (where present), as well as analysis of sediments, necessary if a full understanding of metal distribution in the secondary environment is to be obtained.

Seasonal variations in the metal contents of sediments and waters were investigated, and it will be demonstrated that such variations are present in sediments for all the elements considered at the locality chosen except lead. Furthermore, it will be shown that, for most elements, seasonal variance is greater than can be explained solely in terms of error variance. Similar, significant seasonal variations will be demonstrated for water samples, and the fluctuations observed related to the relative influences of groundwater and surface run-off.

Finally, the data obtained from the main study area, Yarner Wood (see Section 1.3 for locality details), will be interpreted in terms of natural variability in the area. Conclusions will be presented which relate the observed metal distribution in the secondary environment to the presence of old mine workings, to postulated, sub-outcropping mineralisation, and to changes in the physico-chemical conditions in the systems.



### 1.3 AREAS CHOSEN FOR SAMPLE COLLECTION

A part of S.W. England, including the southern part of the Dartmoor granite together with its metamorphic aureole, was chosen as the area from which to collect samples for this study. All map references in this thesis are correct to 100 metres, and therefore the first and fifth digits relate to hundreds of kilometres east and north respectively of the Ordnance Survey grid origin in the South Western Approaches.

Both tin and base metal mineralisation are known in this region (see Fig. 1.1) and therefore the streams draining the region offer the prospect of examining the distribution patterns associated with clastic (tin) and chemical (base metal) dispersion in the secondary environment. The area was not glaciated during the Pleistocene period (see Holmes (1965) Fig. 519) and therefore the complications caused by transported overburden do not apply. Furthermore, the area in question has been extensively studied by MSc students from Leicester University since the beginning of this decade, and therefore a considerable amount of geochemical information was available, even at the commencement of the project. This permitted the selection of streams, for sampling, which were known in advance to have certain geochemical characteristics. The continuation of teaching operations from Leicester in the area throughout the present investigation was also logistically convenient.

In order to achieve optimisation of analytical procedures, five bulk samples, ranging from 30 to over 50 kg in dry weight, were collected from the localities shown on Fig. 1.1. The sites for the collection of these samples were chosen so that the material obtained would be representative of certain environments. Site 0 was intended

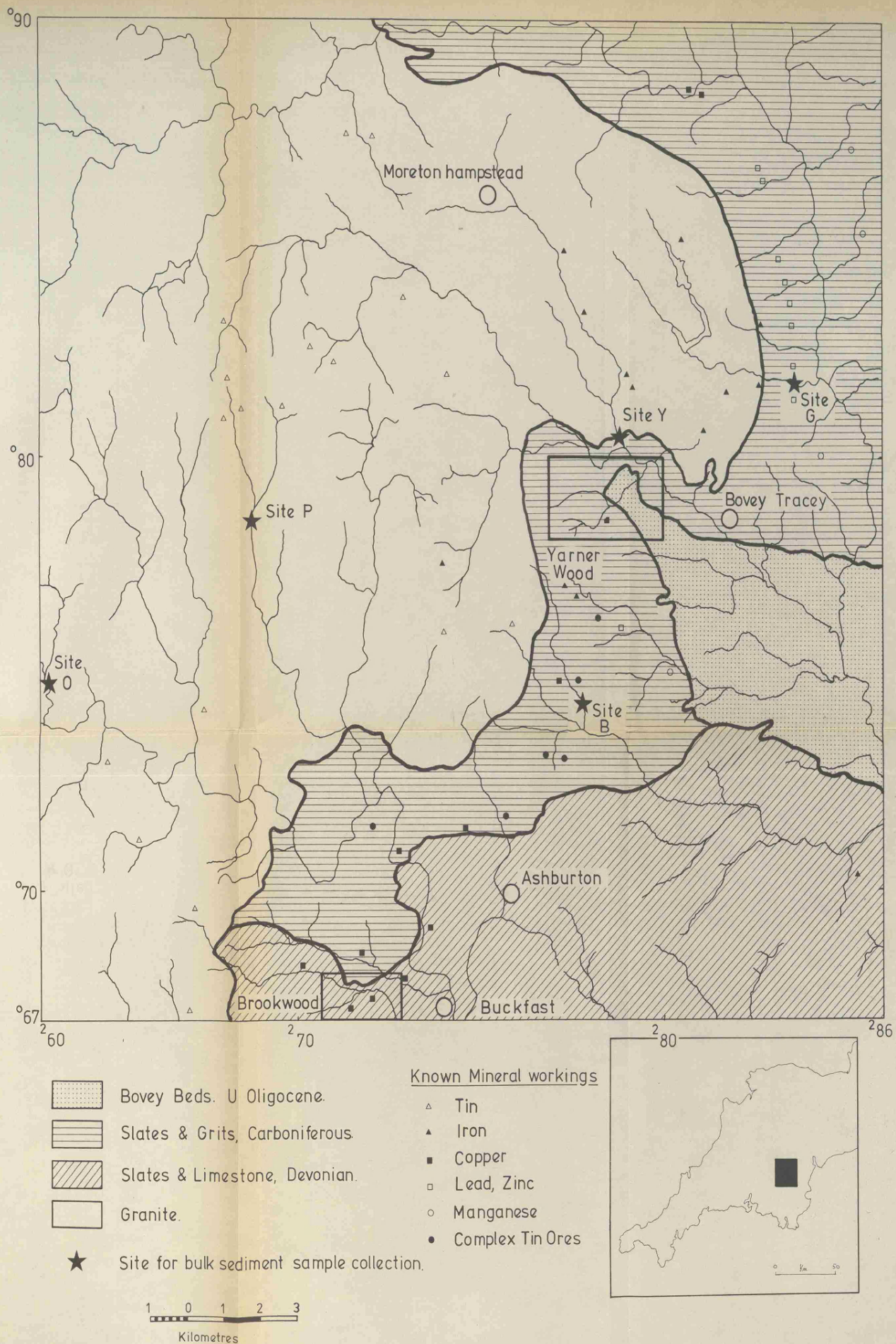
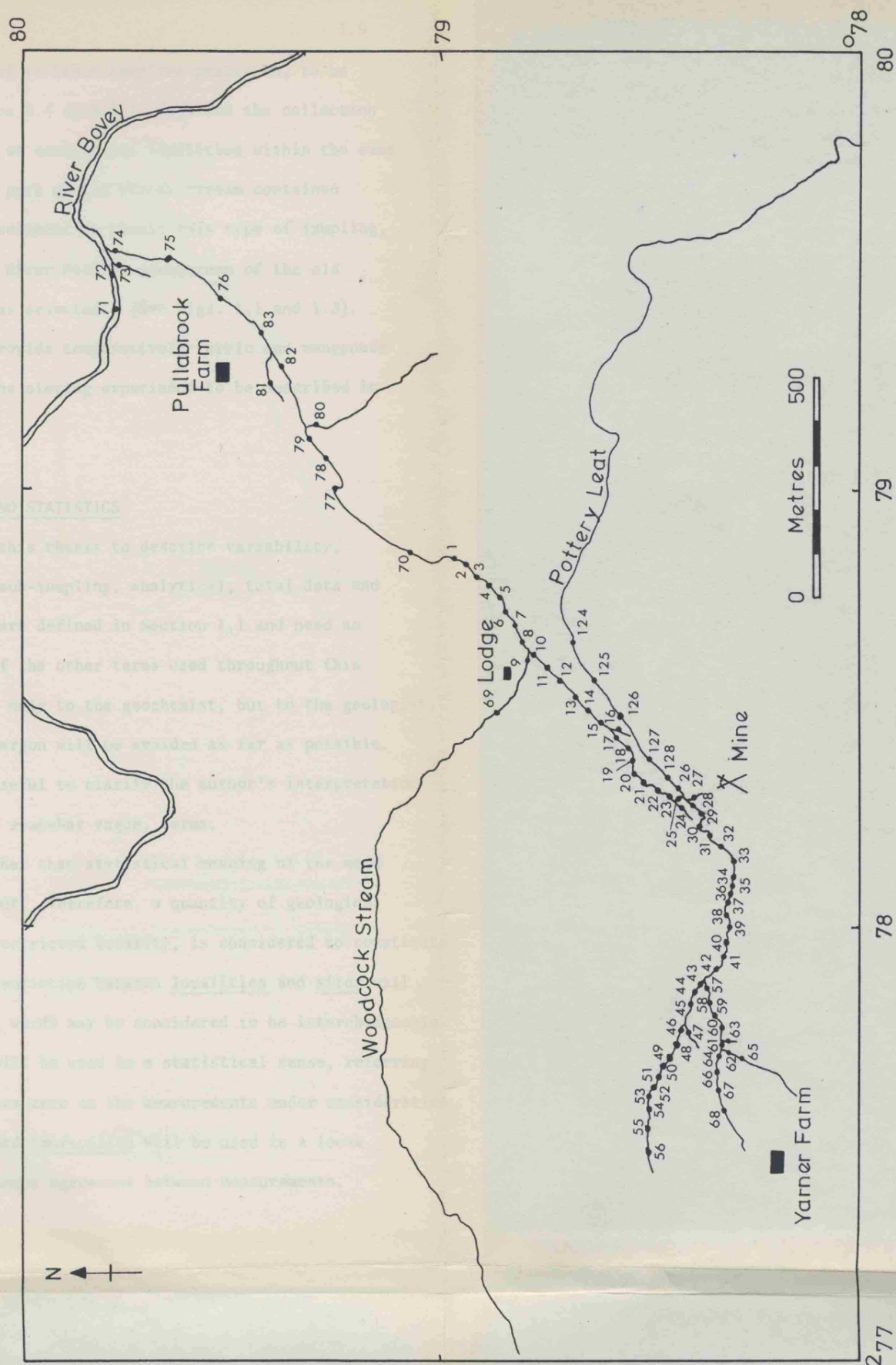


FIG.1-1 MAP TO SHOW LOCATION OF FIELD AREAS & KNOWN MINERALISATION, SOUTH DEVON.

to represent the un-mineralised, granite-derived sediment environment, whilst Site P was intended to represent streams carrying considerable tin values. It was intended that Site B should be representative of base metal mineralisation in the killas (local name for the Devonian/Carboniferous sediments into which the granite was intruded) relatively undisturbed by mining activity, and that Site G should represent base metal mineralisation in the killas contaminated by extensive mining operations. Site Y was selected to represent a background stream with mixed granite and Killas derived sediments. Five hundred millilitre water samples, spiked with various additives, were also collected at three of these sites (B, G & Y) during the same weekend in October 1975.

A number of features contributed to the selection of the Yarner Stream (see Figs. 1.1 and 1.2) as an area for detailed sampling. Sampling of sediments at the road-stream intersection at 27880790 (locality YW1 on Fig. 1.2) had repeatedly revealed anomalous copper and zinc concentrations (C.H. James, pers. comm.) and detailed follow-up work by Harrison (1974) had related this to the presence of old mine workings. In addition, the detailed nature of Harrison's work offered the possibility of a direct comparison between his techniques and those eventually adopted for the present study.

The geology of the area is comparatively straightforward as the headwaters rise on the killas, although some minor degree of complication is introduced by the fact that the lower reaches of the stream are influenced by the presence of the Pliocene Bovey Beds. Upstream of locality YW1 (see Fig. 1.2) the stream flows through the Yarner Wood National Nature Reserve, which means that, as this is a closed Reserve, recent human contamination is very limited.



Sample localities. Prefix Y.W.

FIG. 1.2 SAMPLE LOCALITY PLAN, YARNIER WOOD

FIG. 1.2

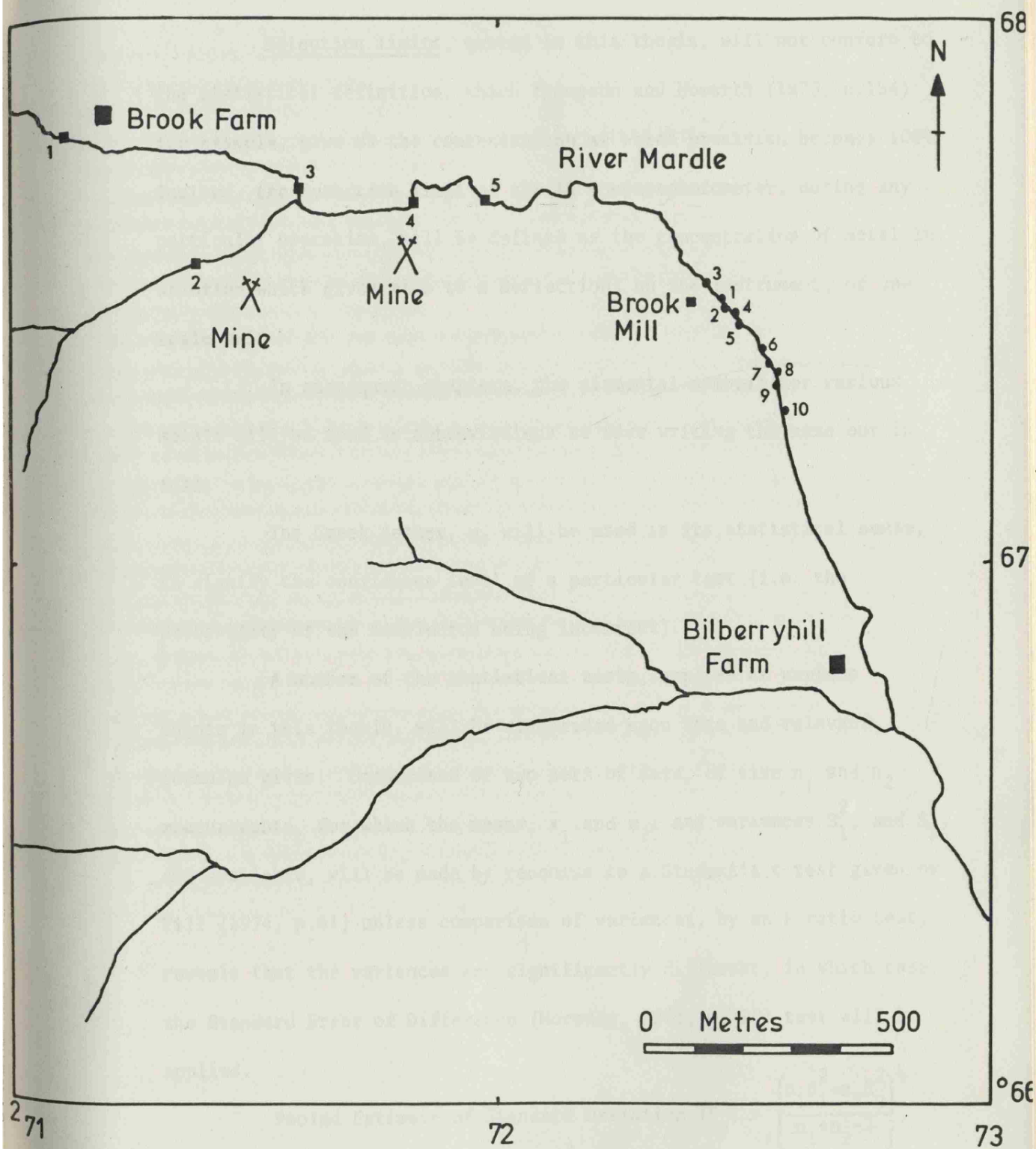
The investigation of variable sampling precision, to be described in detail in Section 3.4 (p.3.21), required the collection of twenty individual samples at each of ten localities within the same small section of stream. No part of the Yarner Stream contained sufficiently large banks of sediment to permit this type of sampling, and, as an alternative, the River Mardle, downstream of the old copper mines at Brookwood, was selected. (See Figs. 1.1 and 1.3). This area was also used to provide comparatively ferric and manganese hydroxide-free samples for the sieving experiment to be described in Section 4.3.3 (p.4.15).

#### 1.4 SOME DEFINITIONS AND STATISTICS

The terms used in this thesis to describe variability, (that is natural, sampling, sub-sampling, analytical, total data and total error variabilities) were defined in Section 1.1 and need no further elaboration. Many of the other terms used throughout this thesis will be familiar, not only to the geochemist, but to the geologist, and the use of unnecessary jargon will be avoided as far as possible. Notwithstanding, it may be useful to clarify the author's interpretation of certain commonly used, if somewhat vague, terms.

The geological rather than statistical meaning of the word sample will be used throughout. Therefore, a quantity of geological material collected at some restricted locality, is considered to constitute a sample. The strict differentiation between localities and sites will not be observed, and the two words may be considered to be interchangeable in this thesis. Precision will be used in a statistical sense, referring to a quantity which approaches zero as the measurements under consideration approach each other. The word imprecision will be used in a loose sense to imply a lack of general agreement between measurements.





3 Sample locality, prefix RM.

5 Sample locality, prefix SV.

FIG.1-3 SAMPLE LOCALITY PLAN, BROOKWOOD

Detection limits, quoted in this thesis, will not conform to the statistical definition, which Thompson and Howarth (1973, p.154) for example, give as the concentration at which precision becomes 100%. Instead, the detection limit of the AA spectrophotometer, during any particular operation, will be defined as the concentration of metal in solution which gives rise to a deflection, on the instrument, of one scale unit.

In subsequent chapters, the elemental symbols for various metals will be used as abbreviations to save writing the name out in full.

The Greek letter,  $\alpha$ , will be used in its statistical sense, to signify the confidence level of a particular test (i.e. the probability of the conclusion being incorrect).

A number of the statistical tests, applied at various points in this thesis, will be elaborated upon here and relevant formulae given. Comparison of two sets of data, of size  $n_1$  and  $n_2$  measurements, for which the means,  $\bar{x}_1$  and  $\bar{x}_2$ , and variances  $S_1^2$ , and  $S_2^2$ , are available, will be made by recourse to a Student's t test given by Till (1974, p.61) unless comparison of variances, by an F ratio test, reveals that the variances are significantly different, in which case the Standard Error of Difference (Moroney, 1953, p.220) test will be applied.

$$\text{Pooled Estimate of Standard Deviation } (S_p) = \left( \frac{n_1 S_1^2 + n_2 S_2^2}{n_1 + n_2 - 2} \right)^{\frac{1}{2}}$$

$$\text{Ratio of variances (F)} = \frac{S_1^2}{S_2^2}$$

(where  $S_1^2 > S_2^2$ ).

$$\text{Student's t Statistic for comparison of means} = \frac{|\bar{x}_1 - \bar{x}_2|}{S_p (1/n_1 + 1/n_2)^{\frac{1}{2}}}$$

$$\text{Standard Error of Difference} = \left( \frac{S_1^2}{n_1} + \frac{S_2^2}{n_2} \right)^{\frac{1}{2}}$$



Use will also be made of the test given by Moroney (op. cit., p.228) for computing a Student's t statistic from the discrepancies between two independent estimates of the same property of the same samples. In this case

$$t = \frac{|\bar{D}| \sqrt{N-1}}{S_D}$$

where  $\bar{D}$  is the mean discrepancy,  
N is the number of comparisons,  
 $S_D$  is the standard deviation of the discrepancies.

### 1.5 ACKNOWLEDGEMENTS

The author's thanks are due to the following:-

to Dr. C.H. James, (my supervisor), for suggesting many of the lines of investigation pursued, and for much helpful discussion and criticism.

to Mrs. V. Rutherford, Miss P. Turner and Mr. C. Mistry for assistance with various aspects of laboratory work.

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to the Nature Conservancy Council for permission to work in Yarner Wood.

to the South West Water Authority and the Meteorological Office for supplying climatic data from the Yarner Wood meteorological station.

to the Natural Environment Research Council, for financial support for 27 months.

Finally, my especial thanks are due to my wife, Linda, without whose moral and financial support this work would never have been begun, let alone finished.

## CHAPTER 2

### OPTIMISATION OF ANALYTICAL TECHNIQUES

#### 2.1 INTRODUCTION

##### 2.1.1. Sample digestion

##### 2.1.2. Particle size and quantity

#### 2.2 DIGESTION TECHNIQUES

##### 2.2.1. General Considerations

##### 2.2.2. Detailed Experiments

###### 2.2.2.1. The effects of different leaches

###### 2.2.2.2. The effect of differing temperatures

##### 2.2.3 Conclusions

#### 2.3 PARTICLE SIZE AND QUANTITY

##### 2.3.1. Design of Experiment

##### 2.3.2. Assessment of experiment

##### 2.3.3. Discussion of results

###### 2.3.3.1. Unseparated samples for Cu,Pb,Zn,Fe,Mn.

###### 2.3.3.2. Unseparated samples for Sn.

###### 2.3.3.3. Heavy and light mineral separates.

##### 2.3.4. Conclusions

CHAPTER 2OPTIMISATION OF ANALYTICAL TECHNIQUES2.1 INTRODUCTION

Any study of natural and error variability in geochemical data must necessitate, firstly, the minimization of analytical imprecisions. However, reduction of such factors to an absolute minimum would result in substantial complication and lengthening of field and analytical procedures, and this negates some of the advantages of applied geochemistry as an exploration technique. Attempts to reduce analytical imprecisions must be conducted within the context of optimisation, striking a balance between reliability on the one hand, and speed and convenience on the other. Some of the factors considered to be important constraints on this type of investigation are discussed below.

2.1.1. Sample digestion

For analysis by either atomic absorption spectrophotometry (AAS) or by colorimetry, samples must be digested into some ultimately liquid form. An investigation of various types of digestion was undertaken in the light of logistical considerations related to common exploration practice (Section 2.2. p.2.3.). The aim of this investigation was to develop a rapid, but efficient, digestion technique which uses readily available materials, under simple, reproducible conditions.

2.1.2. Particle size and quantity

The particle size and quantity of material chosen for analysis is obviously important. The widely held belief that base metals are concentrated in the finer size fractions of a stream

sediment is supported by data from the present study (see Table 2.1)

TABLE 2.1

Mesh size (micron)	Site B			Site G			Site Y		
	Cu	Pb	Zn	Cu	Pb	Zn	Cu	Pb	Zn
-660	47	31	81	407	3740	625	7	22	35
-190	75	55	131	479	6000	483	23	61	86
-140	85	63	140	532	7510	479	27	71	100
-125	91	64	150	632	9290	543	31	78	103
- 70	99	66	167	876	15350	733	40	91	121

0.05g sample weight. All values in ppm. Each value represents mean of 10 replicate determinations.

Therefore it is reasonable to assume that the proportion of metal-rich particles increases as average grain size decreases. This has a substantial effect on the precision of analytical results as will be demonstrated in Section 2.3 (p.2.8.). The overall precision in a field situation also depends on the mesh fraction taken for analysis, as the ratio of coarse to fine particles within the standard minus 190 micron material is bound to vary from site to site. Therefore an ideal analytical procedure will use the finest-grained material present in all samples from the area under investigation. Similar considerations also apply to the selection of a sample weight to be taken for analysis; the greater the sample weight taken, the larger the number of particles and therefore the smaller the imprecision introduced by sub-sampling. Thus, an ideal analytical procedure analyses the largest possible number of the smallest sized particles.

There are drawbacks to this ideal, since the smaller the particle size chosen for analysis, the larger the sample that must be collected in the field which, in turn, is more time-consuming. Table 2.2 illustrates the proportion of minus 70 micron material in the five bulk samples collected.

TABLE 2.2

	<u>Site B</u>	<u>Site G</u>	<u>Site O</u>	<u>Site P</u>	<u>Site Y</u>
Total weight of sample (g)	31,225	38,820	50,420	49,580	40,310
Total weight of -70 micron (g)	432	457	42	455	304
Percentage -70 micron	1.38	1.18	0.08	0.92	0.75

Since such a small percentage of material passes through a 70 micron sieve, bulk samples must be collected in order to obtain a reasonable amount of samples for analysis.

Analyses of samples in excess of 1g weight are inconvenient when undertaken in the test tubes commonly available in many laboratories. A balance needs to be found, therefore, between the particle size and weight of samples taken for analysis which gives good precision, but does not unduly extend field procedures, or require the re-equipping of existing laboratories.

## 2.2 DIGESTION TECHNIQUES

### 2.2.1. General Considerations

Except for cold-extractable As and some Sn determinations, AAS was used throughout this study in preference to Direct Reading Optical Spectrometry (DR Spec.) and colorimetry. The levels of analytical precision obtainable by colorimetry and DR Spec. are less satisfactory than those generally obtainable by AAS. Stanton (1966,p.14)

quotes precisions, at the 95% confidence level and 100 ppm concentration, of 20%, 25% and 10% for Cu, Co and Ni respectively for colorimetric techniques, and at the same confidence level, precisions in the order of 40%, but sometimes as good as 15%, have been quoted by Stanton (1976, p.52) as typical for DR Spec. analysis. In addition, many elements may be determined by AAS from a single digestion. The author, using a twin-beam Perkin Elmer 360 instrument coupled to a Perkin Elmer Digital Volt Meter/Printer, (see Plate 1), was able to determine 10 elements on 120 prepared samples in an 8 hour day. Speed of this sort, coupled with excellent reproducibility, cannot be expected from any of the other analytical techniques available to the author.

The presence of sulphate in solution can lead to chemical interferences when determining some elements, (Welz, 1976, p.101 and 153) and, because of this, bisulphate fusion or sulphuric acid attacks were avoided. Contributory factors to the making of this decision are the extra complexity of using a fusion technique and the potential danger of using sulphuric acid. Thus, a liquid leach technique, excluding the use of  $H_2SO_4$  was chosen.

A thermostatically controlled electric water bath was chosen as a heating medium in preference to a sand bath, or other form of hot air bath. Boiling, or near boiling, water is very readily available as a constant temperature digesting medium, even in the most remote field areas, where bottle gas heated baths may be used.

#### 2.2.2. Detailed experiments

A series of detailed investigations, using minus 190 micron material from bulk- sample sites B, G and Y, was carried out in order to investigate the differing extractive powers of:

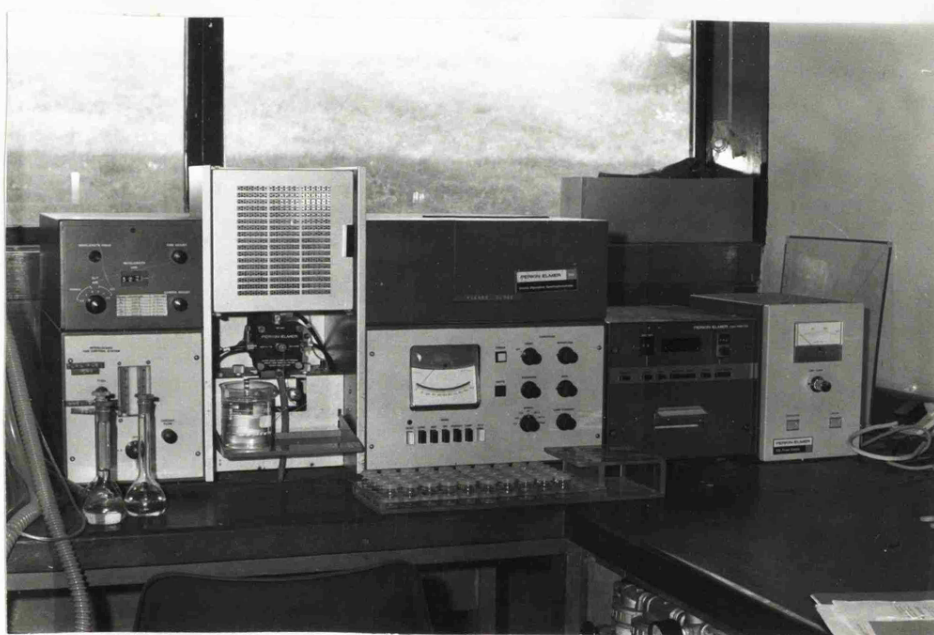


PLATE 1

Perkin Elmer 360 twin-beam Atomic Absorption Spectrophotometer



- (a) various leaching agents,
- (b) solution strengths of leaching agents,
- (c) lengths of digestion time, and
- (d) varying bath temperatures.

#### 2.2.2.1. The effects of different leaches.

An experiment was conducted to compare the efficiency of 10% and 25% (v/v) hydrochloric acid, 25% nitric acid and 10% (w/v) ammonium citrate and hydroxylammonium chloride solution over periods of time up to 96 hours at 60°C. Nine 1 litre conical flasks were used to test the three mineral acids, with 10g of site B minus 190 micron material in each. 500 ml of each acid was put into three flasks, and all 9 flasks, covered to minimise evaporation losses, were kept in a water bath at 60°C for 96 hours. 2 ml aliquots for analysis were removed and diluted to 4 ml with de-ionised water at the following times; (all values in hours)  $\frac{1}{4}$ ,  $\frac{1}{2}$ , 1, 2, 3, 4, 5, 6, 7, 9,  $10\frac{1}{2}$ , 13, 24, 28, 32, 48, 51, 57, 73, 81, 96. 500 ml of acid was used because the removal of 20 x 2 ml aliquots will have only a slight effect on the overall concentration at the end of the experiment.

In another experiment, 24 test tubes, each containing 0.2g of site G minus 190 micron material, were digested for up to 14 hours in 5 ml of the ammonium citrate/hydroxylammonium chloride solution. These were removed in pairs and diluted to 10 ml at the following times; (all times in hours)  $\frac{1}{4}$ ,  $\frac{1}{2}$ , 1,  $1\frac{1}{2}$ ,  $2\frac{1}{4}$ ,  $3\frac{1}{2}$ ,  $4\frac{1}{2}$ , 5, 6, 8, 10, 14.

Figures 2.1, 2.2, 2.3 and 2.4 show the mean Cu and Zn results for each type of leach, plotted against time. All three acids (10% HCl, 25% HCl and 25% HNO<sub>3</sub>) showed a rapid increase in metal content in the solution with time, followed by an asymptotic levelling-off, although the time taken to reach the level portion varied from acid to acid.

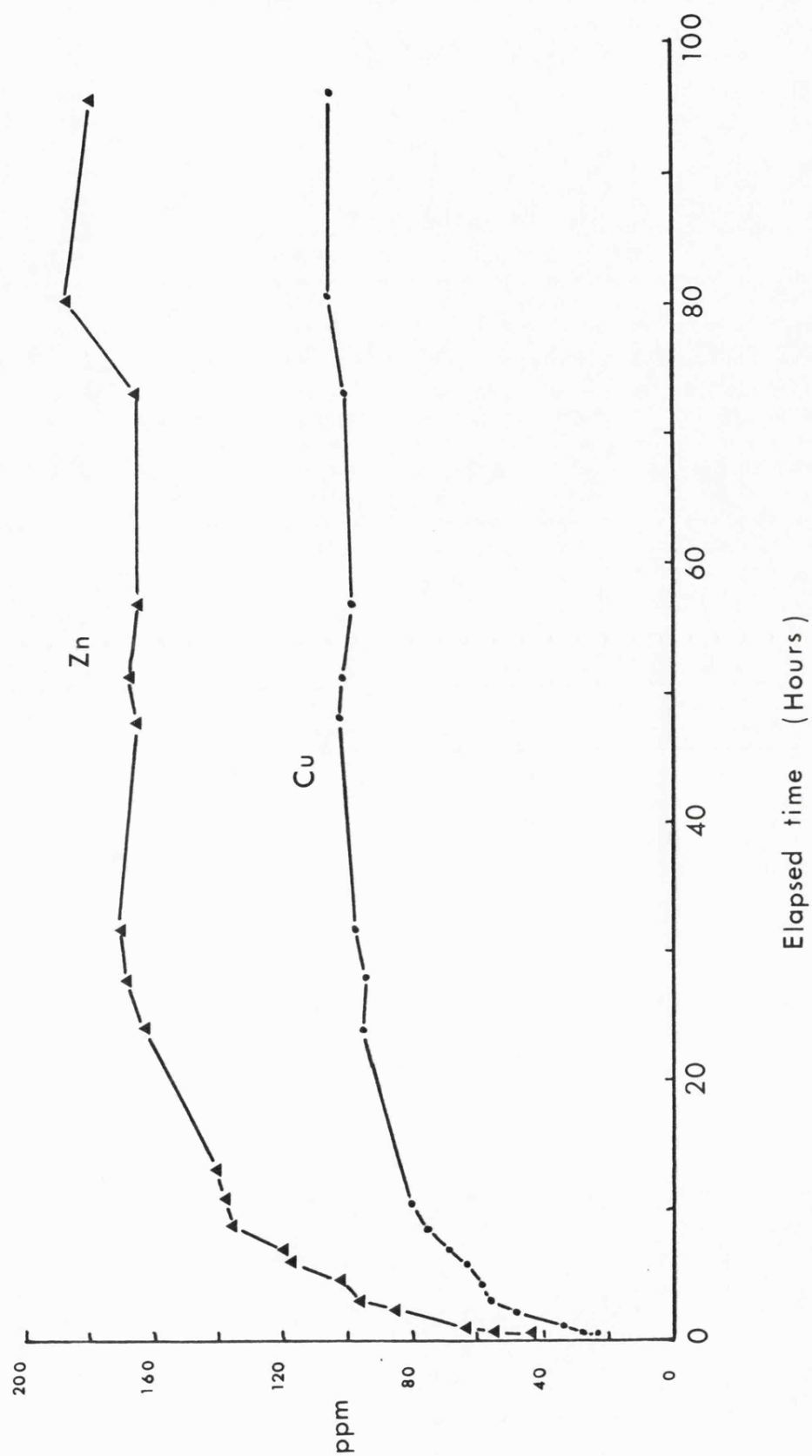


Fig 2.1

Plot of concentration against time. Site B

- 190  $\mu$ , 10% HCl at 60°C.

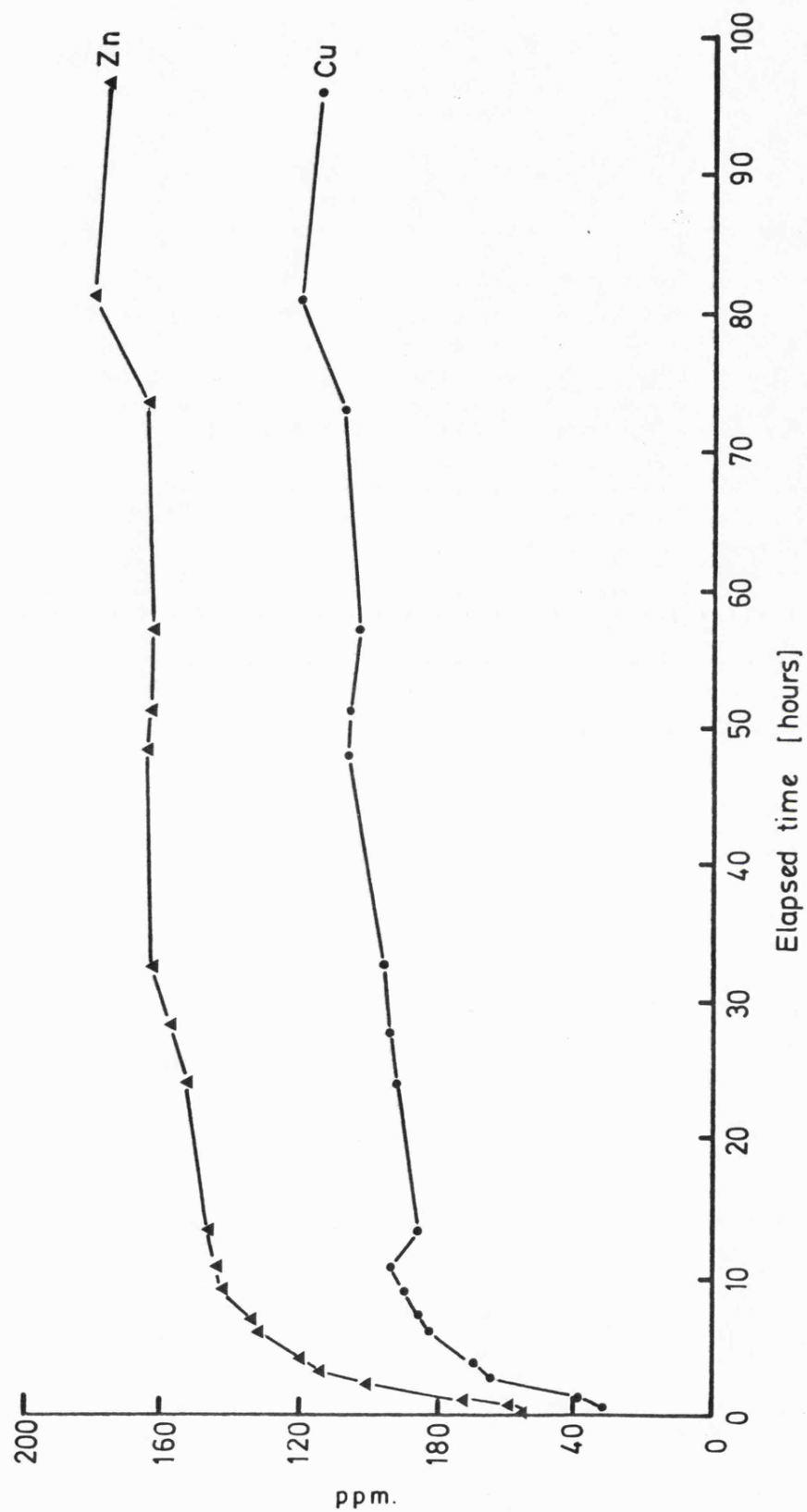


Fig. 2.2 Plot of concentration against time Site B -190 micron,  
25% HCl at 60 °c

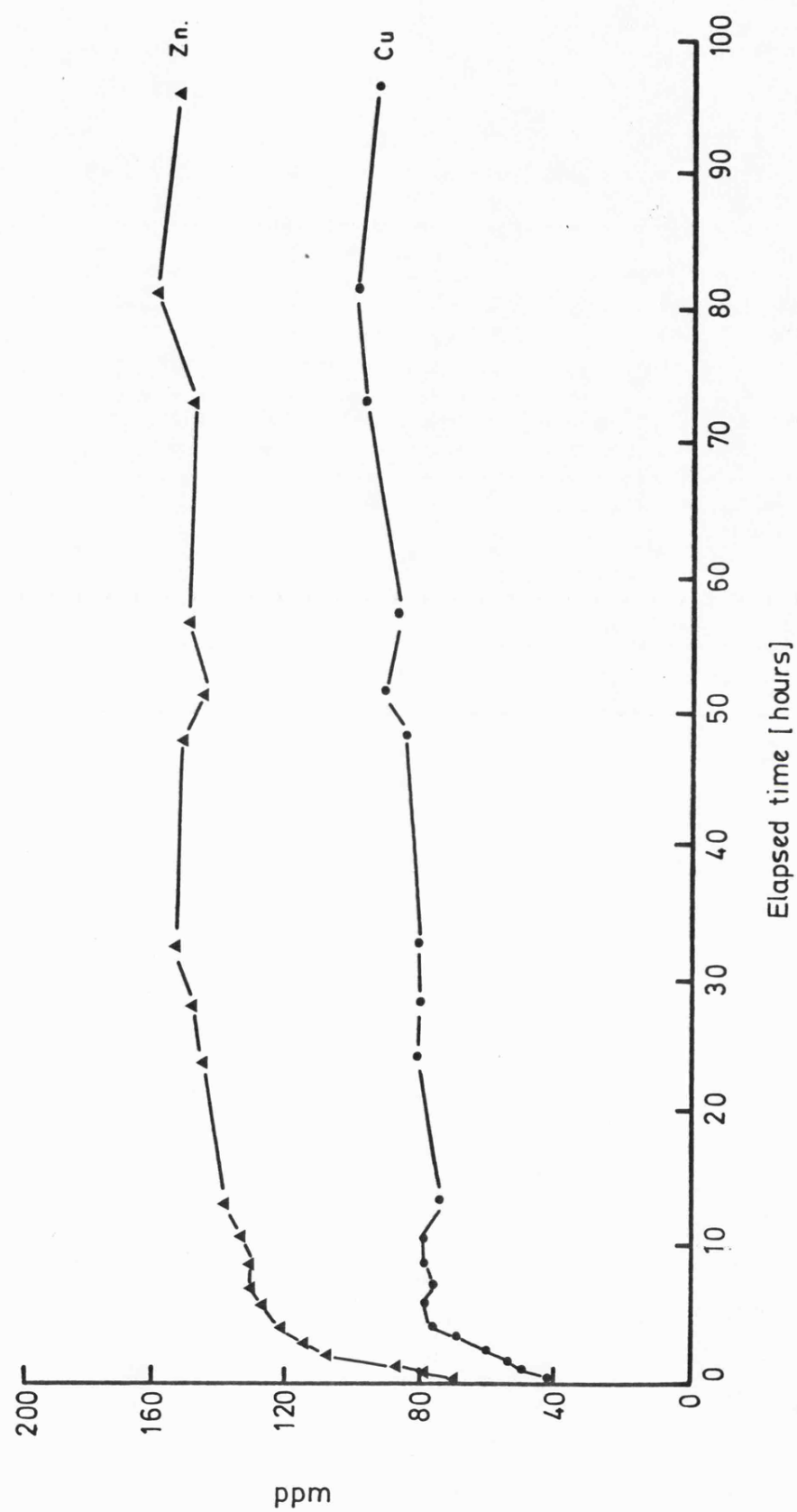


Fig.2-3 Plot of concentration against time. Site  $\beta$ , -190 micron,  
25%  $\text{HNO}_3$  at 60°C

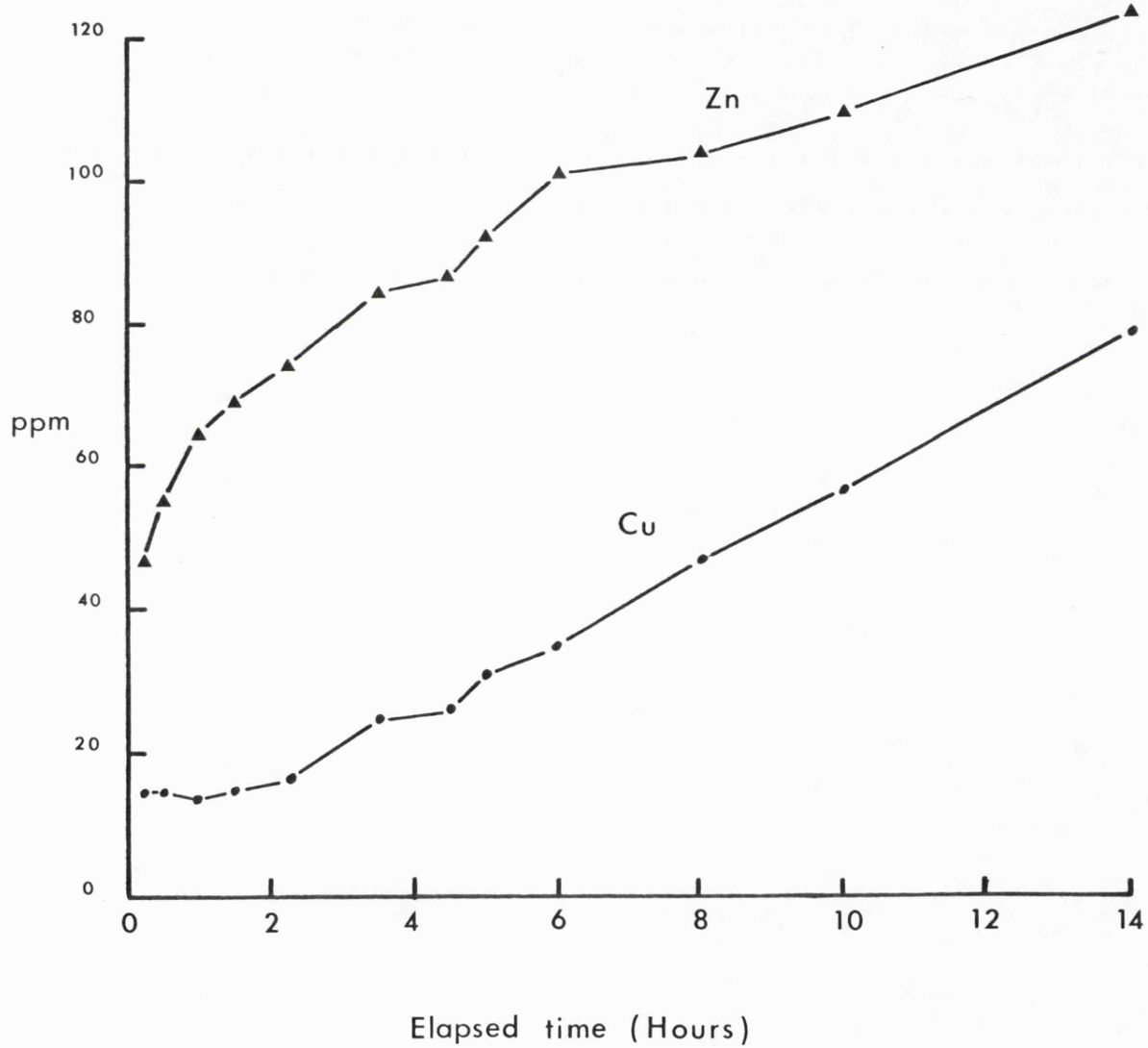


Fig. 2.4 Plot of concentration against time. Site G - 190  $\mu$ . 10% w.v.  
soln. ammonium citrate/hydroxylammonium chloride at 60°C.

Figure 2.1 shows that 10% HCl requires at least 24 hours to reach this state, whilst 25% HCl approaches it in about 15 hours (Fig. 2.2), and 25%  $\text{HNO}_3$  achieves this steady state, (albeit at a slightly lower absolute level) in 4 hours for copper and 12 hours for zinc (Fig. 2.3). The results for the ammonium citrate/hydroxylammonium chloride leach (Fig. 2.4) are less conclusive because the experiment continued for only 14 hours, during which time neither copper nor zinc reached a steady state.

A similar experiment, using minus 190 micron material from sites B and G, was carried out at 95°C, using the three mineral acids (10% HCl, 25% HCl and 25%  $\text{HNO}_3$ ). The results for Cu and Zn are shown in Figures 2.5 to 2.10 inclusive. These demonstrate that the asymptotic levelling off is much more quickly achieved at the higher temperature. Comparison of Figs. 2.6, 2.8 and 2.10 confirms that the level portion is achieved, albeit rather erratically, somewhat more quickly by the 25%  $\text{HNO}_3$  than by the hydrochloric acids.

As part of a more detailed investigation of analytical techniques, described in Chapter 5, a comparison was made, using a 2-way analysis of variance on logarithmically transformed data, between sets of 20 x 0.2g replicates of minus 190 micron material from sites B, G and Y for Cu, Pb, Zn, Fe and Mn after nitric-perchloric acid attack and 25% nitric acid attack. The nitric/perchloric attack involved the addition of 4 ml concentrated  $\text{HNO}_3$  and 1 ml of concentrated  $\text{HClO}_4$ , evaporated to dryness, and then the residue taken up in 5 ml of 50% (v/v) HCl.

The significance of differences in the mean values obtained by each treatment was assessed by reference to Fisher's Least Significant Difference statistic as defined by Till (1974, p.111), and Table 2.3 summarises the results.

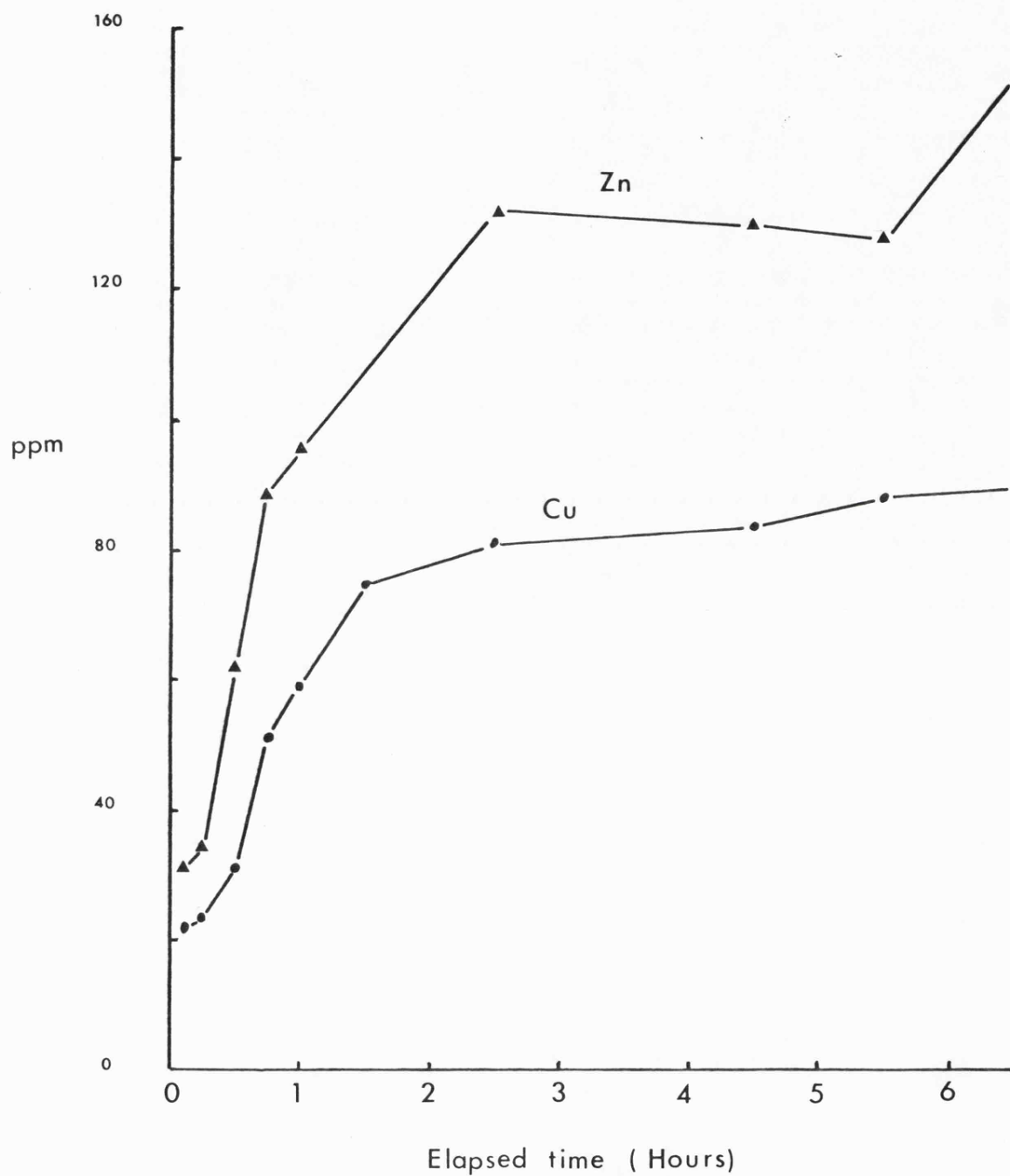


Fig. 2.5 Plot of concentration against time. Site B,  
-190  $\mu$ , 10% HCl at 95°C.

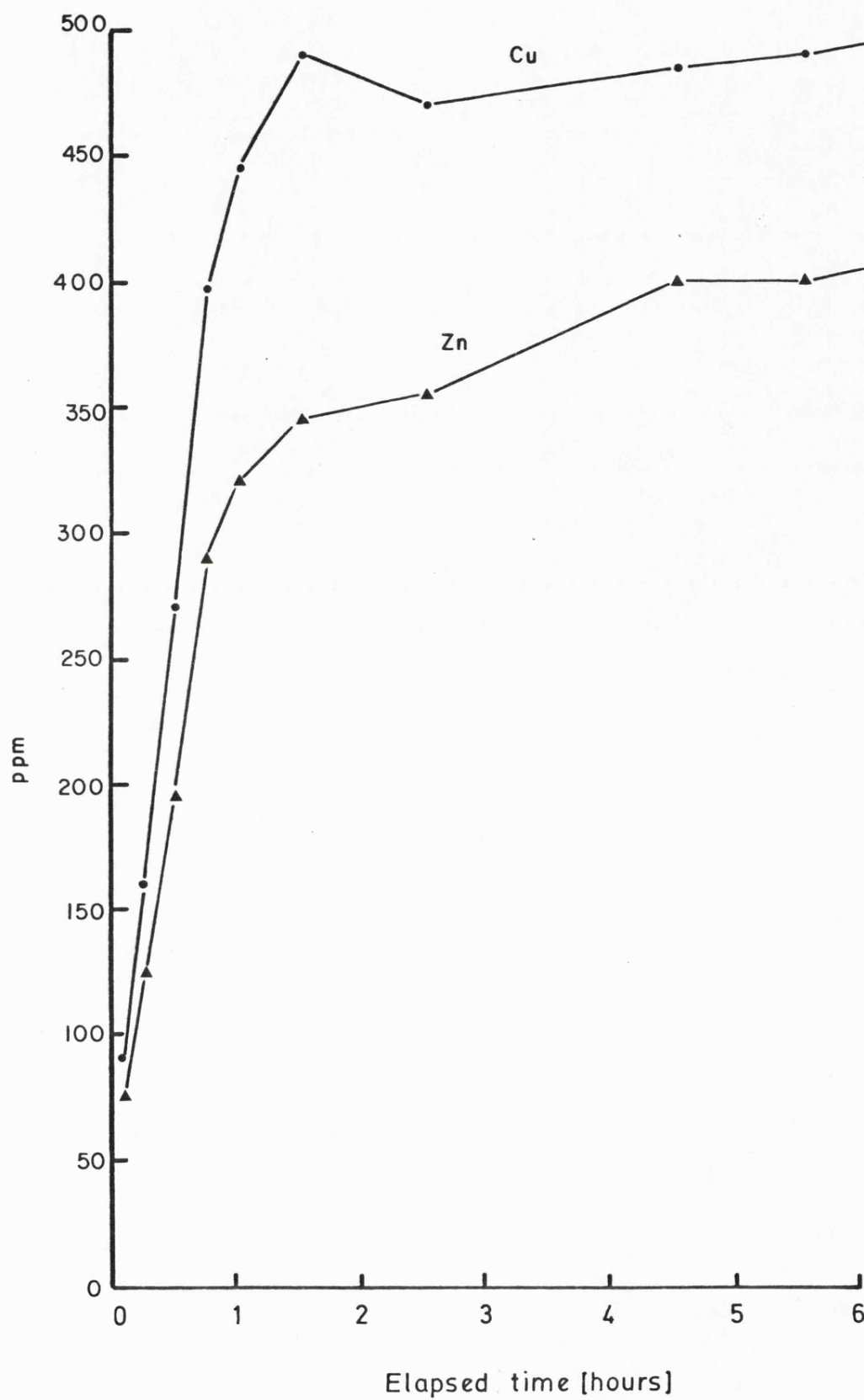


Fig 2-6 Plot of concentration against time. Site G, -190 micron  
10% HCl at 95°C



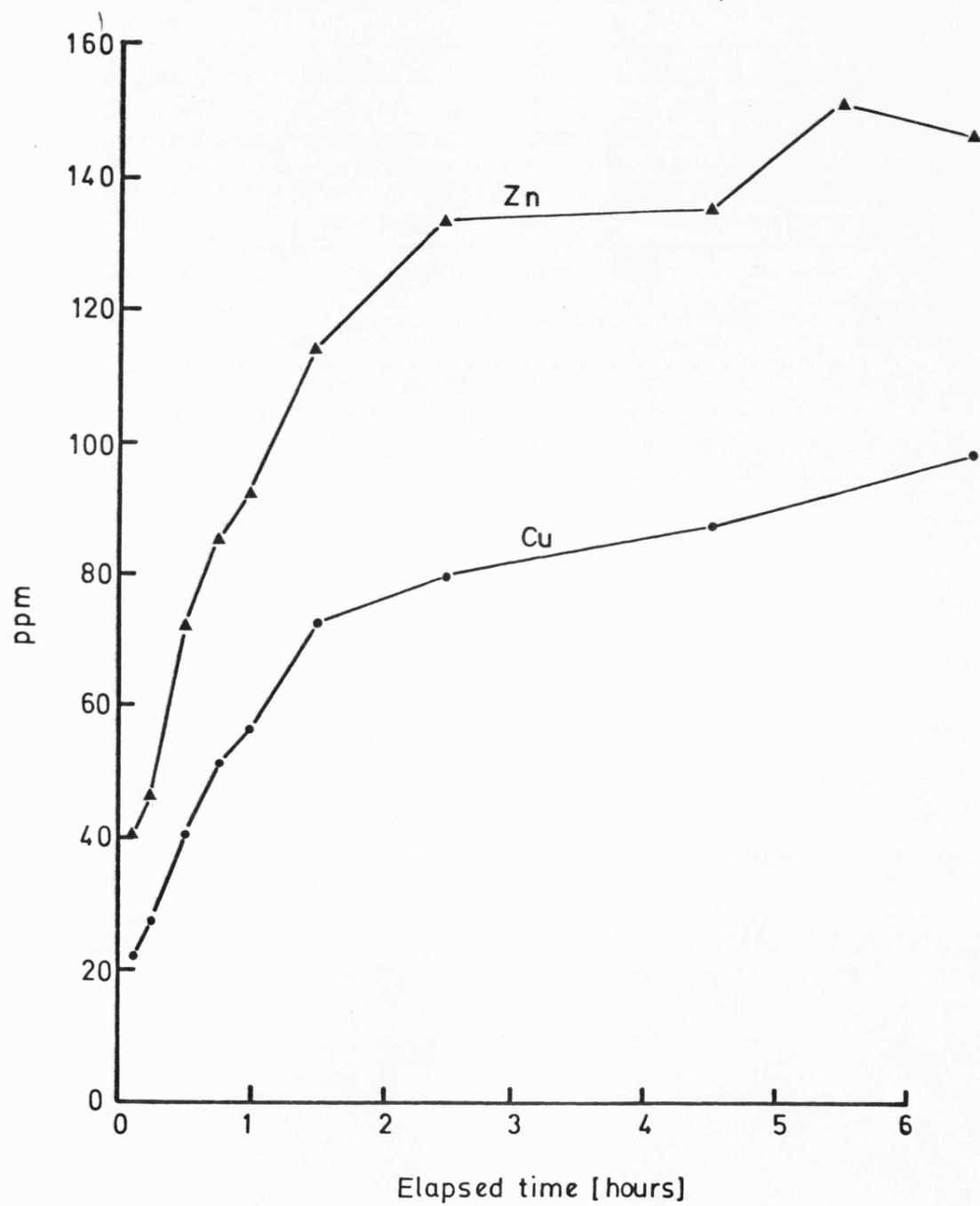


Fig 2:7 Plot of concentration against time. Site B, -190 micron.  
20% HCl at 95°C

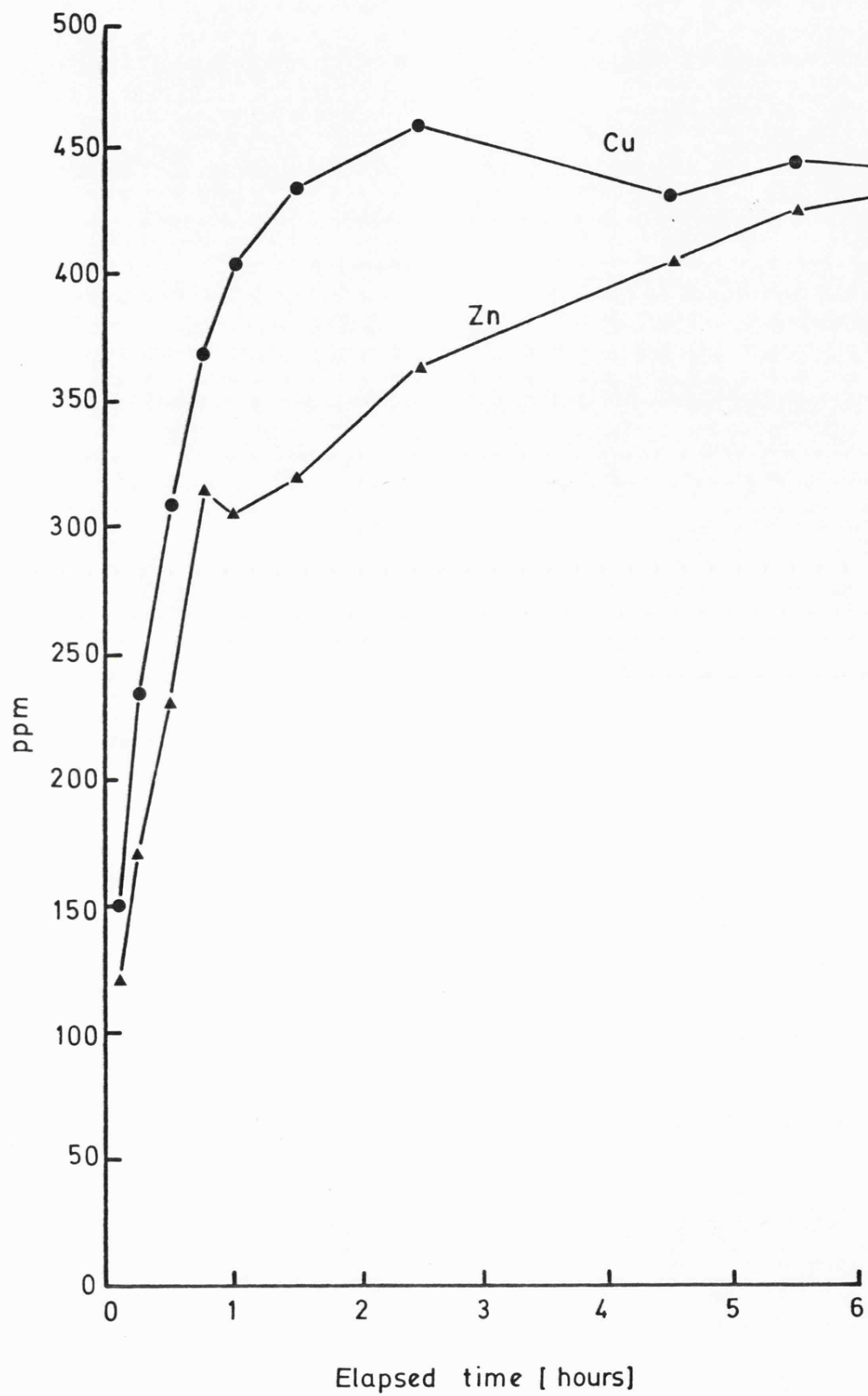


Fig. 2.8 Plot concentration against time, Site G, -190 micron.  
25% HCl at 95°C

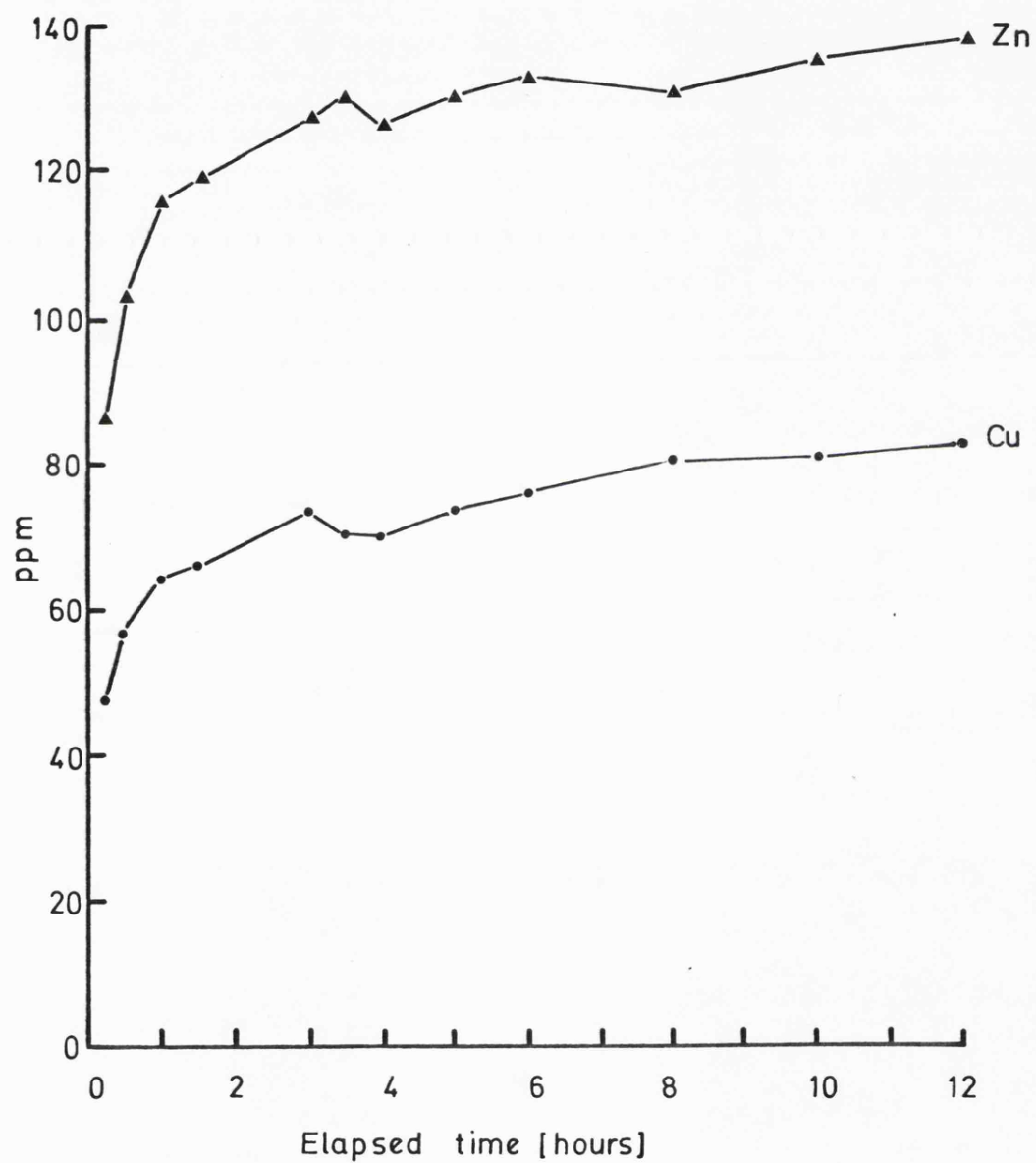


Fig. 2.9 Plot of concentration against time. Site B. -190 micron.  
25% HNO<sub>3</sub> at 95°C

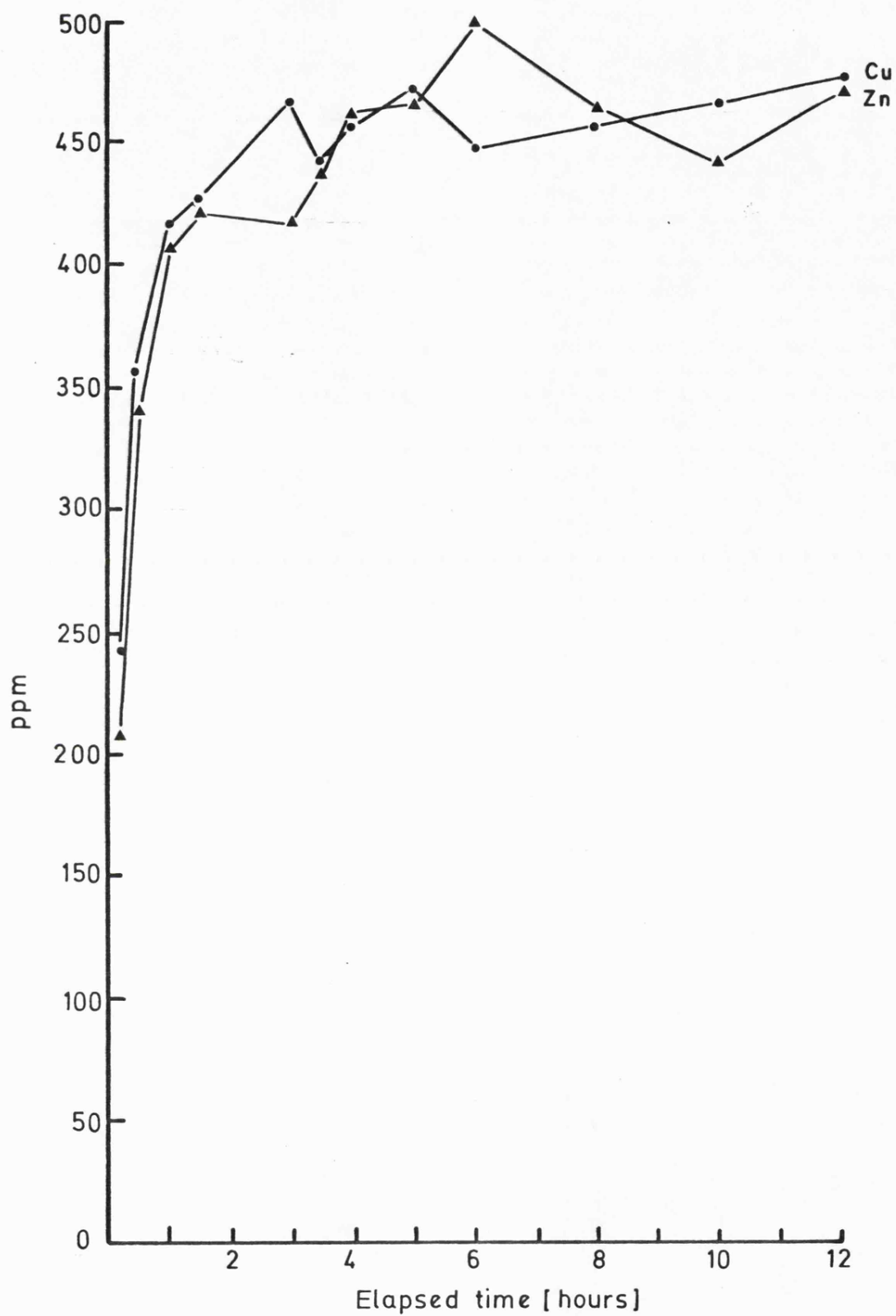


Fig 2.10 Plot of concentration against time. Site G, -190 micron  
25%  $\text{HNO}_3$  at 95°C

TABLE 2.3

Total attack (Nitric/perchloric) compared with partial attack (25%  $\text{HNO}_3$ )

	Cu	Pb	Zn	Fe	Mn
Site B	s	s	s	s	s
Site G	s	ND	ND	s	s
Site Y	ND	ND	ND	s	ND

ND denotes no significant difference in treatment means at  $\alpha = 0.01$ .

s denotes a difference in treatment which is significant at  $\alpha = 0.01$ .

Nine of the fifteen combinations show a significant difference in treatment means and all show higher levels of metal for the nitric/perchloric attack. However, the nitric/perchloric attack is considerably more dangerous, complicated and time-consuming than the 25%  $\text{HNO}_3$  attack and the value of the higher metal extraction is open to some doubt in the context of applied geochemistry.

#### 2.2.2.2. The effect of different temperatures.

A series of experiments was conducted on material from site G, in which 0.2g portions of minus 190 micron sample were leached for up to 28 hours in test tubes with 5 ml of 4M  $\text{HNO}_3$  at 20°C, 60°C and 95°C. The results for Cu, Pb, Zn, Fe and Mn are summarised in Figures 2.11, 2.12 and 2.13. These illustrate, as might be expected, that a steady state of extraction is achieved fastest at high temperature. However, even at 95°C, more than three hours is generally required for 25%  $\text{HNO}_3$  to achieve a steady state of metal content. It is sobering to note that, at the 1 hour digestion interval commonly used in many academic and industrial institutions most of the graphs are rising very

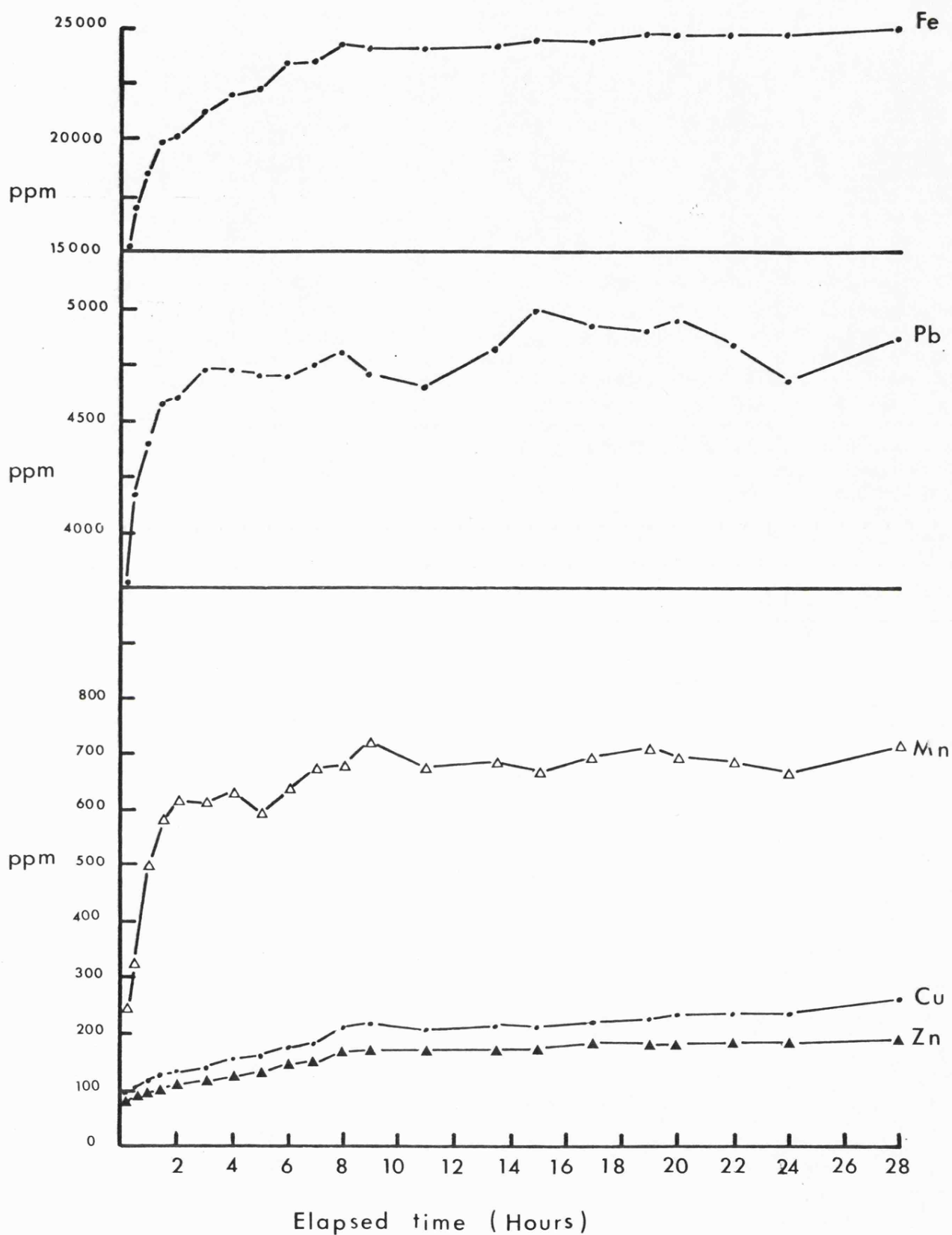


Fig. 2.11 Plot of concentration against time. Site G, - 190  $\mu$

25%  $\text{HNO}_3$  at 20°C.

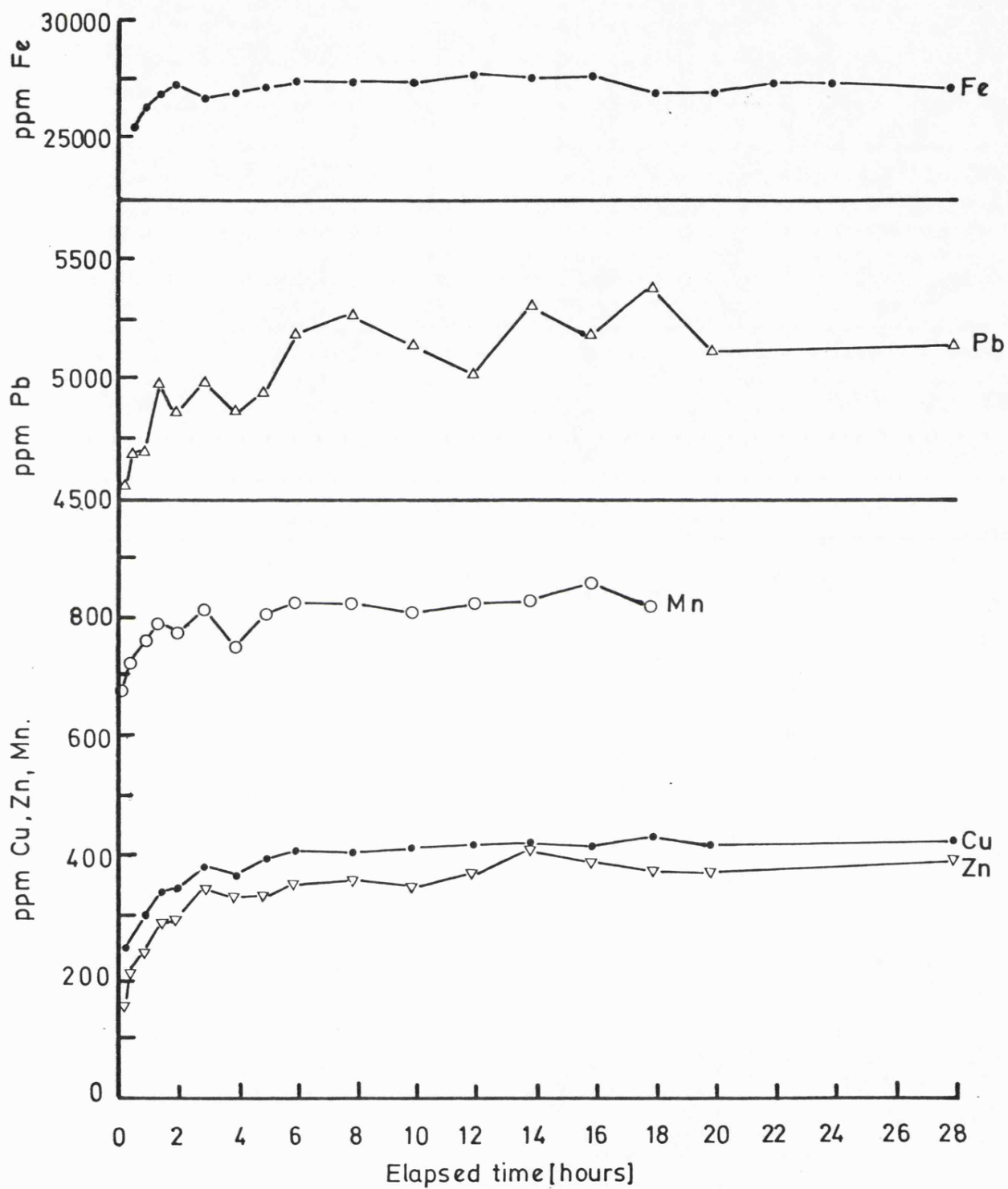


Fig. 2.12 Plot of concentration against time. Si<sub>3</sub>N<sub>4</sub>, -190 micron  
25% HNO<sub>3</sub> at 60°C

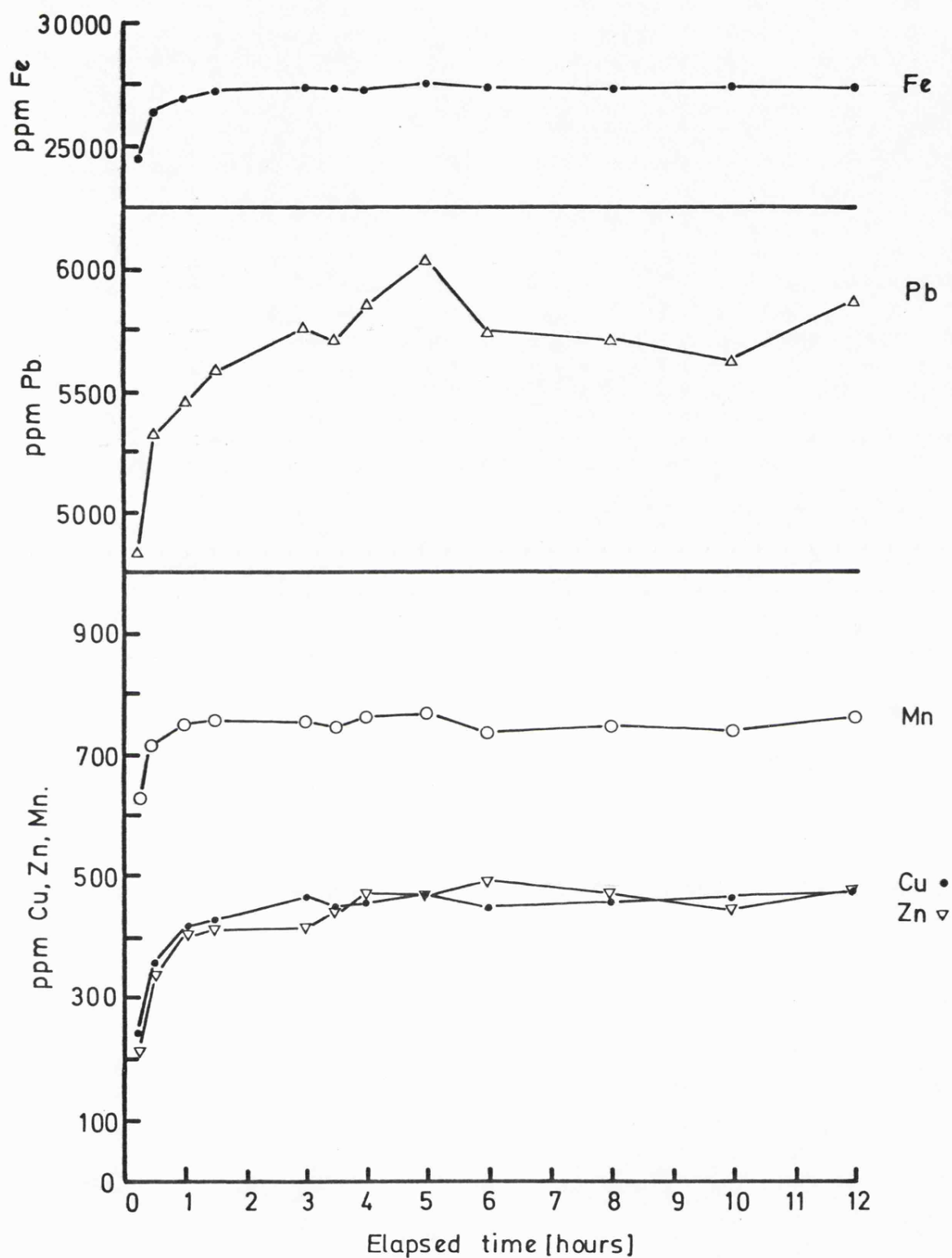


Fig 2.13 Plot of concentration against time. Site G,-190 micron.  
25% HNO<sub>3</sub> at 95°C



steeply. This means that the exact length of time for which samples are left to digest is very critical, if good reproducibility is to be achieved. Furthermore, extraction is generally far from complete even after 2 hours.

### 2.2.3. Conclusions

Consideration of speed and reproducibility has resulted in the selection of AAS as the preferred analytical method wherever possible, necessitating the digestion of the samples, other than by bisulphate fusion and/or sulphuric acid digestions.

25%  $\text{HNO}_3$  has been shown, at fixed temperature, to be a more efficient digestion medium than 10%  $\text{HCl}$ , 25%  $\text{HCl}$  and 10% ammonium citrate/hydroxylammonium chloride solution and a more convenient and rapid, though slightly less rigorous, medium than nitric/perchloric acids.

The speed of digestion can be enhanced by using elevated temperature, but even at  $95^\circ\text{C}$  using 25%  $\text{HNO}_3$ , a 4 hour digestion is necessary to ensure satisfactory extraction. Further elevation of the temperature has not been considered because a hot water bath provides a readily available and reproducible heat source even in the most remote field areas, where an electricity supply, for example, may be intermittent or lacking. Furthermore, acid evaporation losses at temperatures in excess of  $100^\circ\text{C}$  make digestion an impractical technique.

The optimum digestion technique used in this study was therefore 25% (v/v) (4M)  $\text{HNO}_3$  at  $95^\circ\text{C}$  for 4 hours.

## 2.3 PARTICLE SIZE AND QUANTITY

For the reasons outlined in Section 2.1.2, when analysing for elements concentrated in the finer size fractions of a stream sediment, a balance must be found between analysing large amounts of very fine grained material, with high metal content, and low sub-

sampling errors on the one hand, and collecting a realistically sized sample in the field, and using a sub-sample size which conveniently utilizes existing analytical techniques on the other. A series of experiments described below was, therefore, designed to see if such an optimum could be found.

### 2.3.1 Design of Experiment

The dried bulk samples collected at sites B, G, O, P and Y were each sieved and split (see Section 4.3, p.4.11) into ten mesh fractions: (all in microns) -2000 + 660, -660, -660 + 190, -190, -190 + 140, -140, -140 + 125, -125, -125 + 70, -70. It was initially intended that 10 independent replicate analyses should be carried out on each mesh fraction at each of 8 sample weights: 0.05g, 0.1g, 0.2g, 0.3g, 0.5g, 1.0g, 5.0g and 10.0g. However, it became clear, at this point, that the maximum sample weight which can be handled conveniently in test tubes is 1.0g, and so an attempt was made to simulate 5.0g and 10.0g samples by preparing 50 x 1.0g samples and combining 5 x 1 ml and 10 x 1 ml aliquots from each tube in sequence. Whilst this procedure will smooth any variability in the original 50 x 1.0g samples, it does not fulfil the purpose of the experiment, which is to examine variability at different sample weights. Therefore, the results from these simulated samples will not be included in the following discussions.

Material from sites B, G and Y was analysed for Cu, Pb, Zn, Fe and Mn and the initial design of the experiment included analysis for Sn of material from sites O and P. Chapter 5 discusses some of the analytical problems which resulted in the work done being less complete than had been intended.

Some of the fractions from sites B and G were selected for heavy mineral separation in order to see if any substantial advantage

could be gained from analysis of either heavy or light fractions.

A Chas. W. Cook Micropanner (see Plate 2 ) was utilised as a simple, safe alternative to the use of heavy liquids, and for samples of restricted particle size (e.g. -190 + 140 microns, -140 + 125 micron) it appeared to effect a good gravity separation. However, in samples with a wide range of particle sizes, it was obvious that the small sized, heavy particles were carried off with the larger sized lights, as they have similar hydrodynamic properties. It proved to be particularly difficult to effect an adequate separation on mixed coarse and fine grained material and some size fractions were separated using tetrabromoethane (sg 2.96).

### 2.3.2 Assessment of experiment

The applied geochemist does not generally seek accuracy within his results, but rather seeks to obtain results which are precise, and in which the level of precision remains constant throughout an individual survey. Therefore, precision was selected as the parameter with which to assess this particular experiment. Thomson and Howarth (1973) have argued that the traditional measure of precision,  $\frac{198 \times \text{Standard deviation } \%}{\text{mean}}$  at the 95% confidence level, is inappropriate for pairs of measurements such as are commonly used to monitor precision in applied geochemistry. They advocate the use of the estimator  $\frac{400|x_1 - x_2| \%}{x_1 + x_2}$ , where  $x_1$  and  $x_2$  are a pair of observations of some character, the precision of which is to be assessed, because this estimator is sensitive to the absolute level of concentration of the pair of values involved.

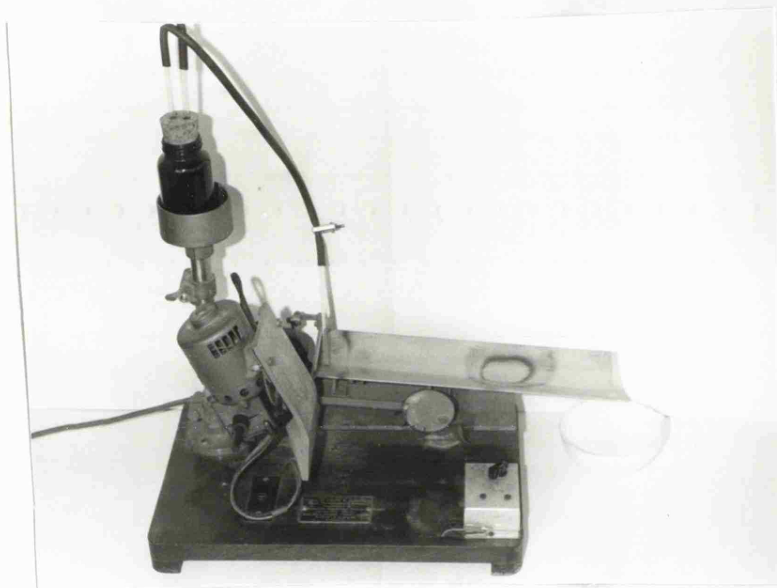


PLATE 2

Chas. W. Cook Ltd. Micropanner

N replications allow the selection of  $T = C_2^N$  ( $T = \frac{N(N-1)}{2}$ ) mutually exclusive pairs of values. Thus T estimates of precision can be made from each batch of N replicates, and an overall estimate of the precision of the batch of N can be obtained from the mean of the T estimates. A FORTRAN computer program, TOMHOW, was written to compute precision estimates from the base 10 logarithms of N replicate determinations (see Appendix 1 for program and specimen printout), and it is this data which is displayed as Tables 2.4, 2.5, 2.6, 2.7, 2.8, 2.9, 2.10, 2.11 and 2.12.

### 2.3.3 Discussion of results

#### 2.3.3.1 Unseparated samples for Cu, Pb, Zn, Fe, Mn.

Examination of the data in Tables 2.4, 2.5 and 2.6 shows that, as anticipated, precision generally improves as larger quantities of finer-grained materials are analysed. However, some more objective form of discrimination was sought in order to aid the selection of an optimum sample weight and particle size.

The object of this experiment is to determine at what minimum mesh size and sample weight sub-sampling error can be shown to be indistinguishable from analytical error. In the case of AAS, the latter can be assessed by making duplicate readings on the same liquid, subsequently referred to as re-reading error. Thus, a precision value attributable only to re-reading error can be calculated for each re-reading pair and for each element sought. The numbers of duplicate readings are tabulated in Table 2.13.

TABLE 2.4

Site B. Mean of precision estimates for each set of conditions.

N = number of replicates = 10 in each case.

-70 micron

	0.05g	0.1g	0.2g	0.3g	0.5g	1.0g
Cu	2.2	1.7	1.7	2.9	1.5	1.3*
Pb	9.8	5.6*	2.2*	1.3*	1.6*	1.8*
Zn	2.9	1.5	1.3	0.8*	1.1	0.6*
Mn	1.6	1.2	0.7*	0.5*	0.4*	0.6*

-125 + 70

Cu	4.7	2.0	2.0	1.4	1.3*	2.5
Pb	10.5	7.1	2.7*	3.7*	3.9*	2.9*
Zn	3.0	2.2	1.4*	0.6*	1.2*	1.7
Mn	4.3	1.8	0.6*	0.8*	1.8	1.7

-125

Cu	2.4	1.5	1.9	1.7	1.9	1.0*
Pb	4.7*	4.7*	1.5*	2.8*	2.0*	1.6*
Zn	1.5	0.8*	2.4	1.2	1.1*	0.9*
Mn	2.6	1.6	1.3	1.0	0.4*	0.7*

-140 + 125

Cu	6.5	3.2	2.0	2.4	2.2	1.6
Pb	13.7	6.0	3.0*	7.3	4.9	2.1*
Zn	4.5	2.5	3.1	2.1	1.2*	1.5*
Mn	1.3	2.7	1.5	1.3	1.1*	0.9*

-140

Cu	1.6	5.0	1.2*	1.2*	1.6	1.0*
Pb	5.5*	3.5*	4.0*	2.8*	2.9*	1.7*
Zn	1.3	1.3	1.4*	1.1*	1.6*	0.6*
Mn	2.6	2.0	1.1	0.7*	1.1	1.0

-190 + 140

Cu	3.5	2.5	4.7	2.9	2.1*	1.8*
Pb	24.4	7.2	10.1	6.4	8.3	3.5*
Zn	3.0	1.6*	3.2	1.8	1.3*	2.3
Mn	3.1	2.3	1.5	1.5	1.4	1.5

-190

Cu	2.2	4.0	1.4	1.9	2.6	4.6
Pb	11.3	8.5	5.2	3.9*	2.9*	1.7*
Zn	1.2*	1.6*	2.0	1.1*	0.8*	1.2*
Mn	1.1	1.0	1.3	0.9*	0.9*	1.0*

-660 + 190

Cu	13.8	8.3	8.7	6.1	5.2	4.0
Pb	41.4	22.4	17.8*	20.3*	5.9*	11.3*
Zn	4.9	2.8	2.8	3.3	1.5*	3.7
Mn	7.7	8.1	3.3	1.5	1.7	2.2

TABLE 2.4 continued over ...

TABLE 2.4 continued

2.13

-660

	0.05g	0.1g	0.2g	0.3g	0.5g	1.0g
Cu	4.2	5.6	1.6*	3.2	5.8	3.4
Pb	33.7	12.4	16.8	17.5	9.1	4.4
Zn	3.0	3.7	2.0	2.2	1.3*	1.9
Mn	5.0	2.2	1.7	1.2	1.4	3.5

-2000 + 660

Cu	47.7	14.3	21.9	14.7	13.6	12.8
Pb	40.5	66.7	28.6	14.9*	18.5*	5.1*
Zn	19.7	10.4	13.8	7.8	6.0	5.2
Fe	5.9	3.3	1.4	0.7	0.9	0.4*
Mn	22.1	17.4	7.5	8.5	7.4	5.8

\* denotes precision level significantly low.

TABLE 2.5

Site G. Mean of precision estimates for each set of conditions.

-70 micron.

	0.05g	0.1g	0.2g	0.3g	0.5g	1.0g
Cu	1.1*	0.6*	1.2	0.9*	0.8*	1.2
Pb	0.5*	0.5*	0.7*	0.8	0.6*	1.7
Zn	0.5*	0.7*	1.2	1.0*	1.0*	1.2
Fe	0.4*	0.3*	0.7	0.8	0.5*	0.8
Mn	1.0*	0.6*	0.6*	0.5*	0.9*	1.2

-125 + 70

Cu	1.8	1.6	1.1	1.1	1.2	1.2
Pb	0.7*	0.7*	0.7*	0.7*	0.8	0.6*
Zn	5.4	2.7	2.9	1.2	1.5	1.0*
Fe	0.7	0.5*	0.5*	0.5*	0.6	0.7
Mn	2.1	1.0*	0.8*	1.1*	0.9*	0.9*

-125

Cu	1.0*	0.9*	0.9*	0.7*	1.0*	1.7
Pb	0.6*	0.4*	0.5*	0.5*	0.7*	1.6
Zn	2.2	1.9	1.7	0.7*	1.2	2.0
Fe	0.4*	0.5*	0.4*	0.3*	0.5*	1.2
Mn	0.8*	1.0*	0.7*	0.7*	0.5*	1.9

-140 + 125

Cu	2.8	2.5	1.7	1.9	1.5	1.9
Pb	2.1	1.2	0.8	1.2	1.0	1.1
Zn	9.0	6.7	4.7	4.6	2.5	2.5
Fe	0.7	0.8	0.9	0.9	0.6	0.9
Mn	2.6	2.6	1.4	1.1*	0.9*	1.9

-140

Cu	2.4	1.3	1.9	1.4	2.1	1.9
Pb	0.6*	0.9	0.6*	0.8	1.4	1.6
Zn	3.0	2.4	1.8	2.4	2.6	2.1
Fe	0.6	0.5*	1.2	0.6	1.2	1.1
Mn	2.1	2.2	1.1*	1.0*	1.1*	2.2

-190 + 140

Cu	6.4	4.3	2.4	2.2	2.8	2.0
Pb	1.5	1.8	1.2	1.7	1.9	1.4
Zn	9.5	8.1	5.0	5.8	4.3	3.6
Fe	1.0	0.8	1.0	1.2	1.3	1.1
Mn	6.6	2.2	2.3	2.0	1.4	1.4

TABLE 2.5 continued over ...



TABLE 2.5 continued ...

	0.05g	0.1g	0.2g	0.3g	0.5g	1.0g
<b>-190</b>						
Cu	2.2	2.1	1.7	1.3	2.5	1.0
Pb	0.8	0.9	1.1	1.0	1.4	0.6*
Zn	7.3	6.9	7.1	2.5	3.4	2.2
Fe	0.8	0.6	1.1	0.8	0.9	0.6
Mn	2.8	1.6	1.8	1.2	2.0	1.4
<b>-660 + 190</b>						
Cu	16.0	10.8	7.2	8.2	5.7	8.0
Pb	15.8	6.8	3.0	4.6	2.8	1.7
Zn	23.5	24.0	17.1	16.6	15.3	9.0
Fe	4.7	2.5	1.8	1.6	1.5	0.7
Mn	16.0	8.5	7.4	5.0	4.7	2.7
<b>-660</b>						
Cu	11.3	6.5	10.5	8.7	6.0	4.7
Pb	2.9	2.7	3.1	2.1	2.0	1.7
Zn	13.8	32.4	17.5	8.1	10.8	10.1
Fe	2.1	2.5	2.5	1.1	1.0	1.0
Mn	6.7	6.3	6.5	3.2	3.2	3.9
<b>-2000 + 660</b>						
Cu	43.0	20.8	16.0	16.0	15.8	7.3
Pb	24.2	11.5	17.8	11.0	13.5	9.7
Zn	31.9	34.6	18.5	30.1	16.7	17.2
Fe	14.5	5.9	6.2	6.2	4.0	4.2
Mn	34.5	26.1	18.8	7.4	14.6	12.5

N = 10

\* Denotes precision level significantly low.

TABLE 2.6

Site Y. Mean of precision estimates for each set of conditions.

-70 micron

	0.05g	0.1g	0.2g	0.3g	0.5g	1.0g
Cu	5.9	3.1	1.6*	2.2	1.9*	1.6*
Pb	3.9*	2.9*	2.6*	1.7*	1.2*	1.6*
Zn	3.6	1.0*	1.1*	1.4*	1.1*	1.0*
Fe	0.8	0.4*	0.6	0.6	0.5	0.9
Mn	1.0	0.7*	0.9*	1.2	0.5*	1.0

-125 + 70

Cu	5.9*	7.2*	8.3*	3.8*	3.2*	3.5*
Pb	6.5	4.8*	3.6*	3.2*	2.8*	2.2*
Zn	2.8	1.8	2.9	2.4	1.7	1.4*
Fe	0.6	0.7	0.9	1.0	0.8	1.1
Mn	1.8	1.6	1.9	1.9	1.2*	1.8

-125

Cu	5.6*	5.7*	4.7*	4.0*	2.3*	3.3*
Pb	4.8*	5.1*	3.6*	2.1*	1.9*	3.2*
Zn	1.9	1.3*	1.2*	1.6*	1.6*	1.9
Fe	0.4*	0.7	0.9	0.7	0.7	1.0
Mn	1.2	1.3	0.9*	1.2*	1.2*	1.4

-140 + 125

Cu	13.7	13.4	14.5	7.9*	11.4	9.1
Pb	6.3	11.5	13.1	7.3	4.6	4.2*
Zn	2.1	2.8	3.5	2.5	3.1	2.2
Fe	1.1	0.7	0.6	0.7	0.6	0.8
Mn	2.3	2.1	1.5	1.4	1.2*	0.9*

-140

Cu	10.0	6.9*	5.1*	7.7*	5.0*	2.6*
Pb	8.2	4.4*	3.4*	5.0*	2.7*	2.4*
Zn	4.8	1.6*	1.6*	1.6*	1.5*	1.1*
Fe	0.8	0.9	0.7	0.5	0.6	1.0
Mn	1.5	1.2*	1.4	0.9*	0.6*	0.7*

-190 + 140

Cu	12.7	12.0	29.1	3.3*	26.6	17.9
Pb	16.6	4.1*	15.7	13.2	4.8	7.9
Zn	3.8	3.5	6.4	2.7	5.1	2.9
Fe	1.0	0.9	0.7*	1.0	0.7*	0.6*
Mn	2.3	1.8	1.7	1.9	1.4	1.6

TABLE 2.6 continued ...

TABLE 2.6 continued ...

	0.05g	0.1g	0.2g	0.3g	0.5g	1.0g
-190						
Cu	6.2*	7.3*	3.6*	8.6*	4.1*	2.7*
Pb	7.7	5.4	5.6	2.5*	2.0*	3.9*
Zn	2.1	4.2	1.9	1.5*	3.7	2.0
Fe	1.0	1.3	0.7	1.1	0.6	0.8
Mn	1.2*	0.7*	0.8*	1.2*	1.0*	1.3
-660 + 190						
Cu	60.1	32.6	23.4	11.4	11.4	14.7
Pb	24.4	28.7	48.2	15.3*	6.7*	4.0*
Zn	9.8	7.3	28.4	4.1	4.2	3.5
Fe	6.2	3.5	1.9	2.3	1.6	0.8*
Mn	7.6	3.7	3.1	2.6	2.7	0.6*
-660						
Cu	39.1	15.7	14.4	19.0	12.9	8.1*
Pb	27.5	22.7	14.7*	15.0*	13.3*	8.4*
Zn	4.6	7.9	3.9	3.5	5.2	3.3
Fe	4.0	2.6	1.2	1.6	1.3	0.7*
Mn	5.2	4.5	2.3	8.4	6.2	2.4
-2000 + 660						
Cu	95.0	56.3	35.7	56.8	29.2	10.2
Pb	39.3	14.0*	14.2*	16.0*	9.6*	35.0
Zn	14.0	11.6	12.2	20.3	9.6	10.1
Fe	13.3	6.4	6.4	6.4	4.8	2.2
Mn	18.1	26.8	10.2	11.9	7.5	9.6

N = 10

\* Denotes precision level significantly low.

TABLE 2.7

Site 0 for tin. Precision values from TOMHOW (in %)

Size (microns)	0.05g	0.1g	0.2g	0.3g	0.5g	1.0g
-660	ND	100+	76.5	39.9	28.9	22.5
-660+190	ND	7.5	58.5	52.1	40.7	32.2
-190	22.8	15.7	2.7	1.8	ND	ND
-190+140	ND	14.0	9.5	7.1	ND	ND
-140	ND	11.7	4.9	6.6	ND	ND
-140+125	21.4	8.9	6.3	4.4	ND	ND
-125	9.1	3.5	4.9	ND	ND	ND
-125+70	13.4	4.9	3.2	2.4	ND	ND
-70	11.5	12.5	4.6	ND	1.8	1.5

N = 10

ND denotes Not Determined.

TABLE 2.8

Site P. for tin. Precision values from TOMHOW (in %)

Size (microns)	0.05g	0.1g	0.3g	0.5g	1.0g
-660	15.2	2.8	1.3	2.4	2.0
-660+190	13.0	10.8	4.9	1.4	1.2
-190	1.3	1.9	1.2	0.4	0.6
-190+140	3.2	3.0	5.7	4.7	5.9
-140	2.6	1.9	2.5	5.7	4.7
-140+125	3.3	1.9	2.7	3.6	4.1
-125	1.5	2.4	3.0	5.7	2.4
-125+70	3.5	3.2	3.0	3.4	5.1
-70	2.3	1.7	5.3	5.7	5.5

N = 10

TABLE 2.9

Site B. Heavy mineral separates.

-70 micron M

	0.05g	0.1g	0.2g	0.3g	0.5g
Cu	6.6	2.9	1.8*	11.2	7.2
Pb	23.4	10.0	11.2	1.9*	6.1
Zn	2.9	1.1*	0.8*	4.8	2.7
Fe	0.8	0.4*	0.6	1.0	0.9
Mn	6.0	1.4	1.4	1.8	0.4*

-125+70 M

Cu	12.7	6.6	4.9	5.1	7.8
Pb	47.0	16.1	11.8	18.5	7.6
Zn	10.3	4.4	3.3	5.3	2.5
Fe	0.9	0.9	0.8	1.2	2.2
Mn	3.2	2.1	1.6	1.7	1.7

-125 M

Cu	8.2	7.7	3.8	3.7	9.5
Pb	52.6	7.7	7.3	6.0	1.7*
Zn	4.0	1.2*	6.1	3.1	4.1
Fe	1.2	1.7	0.9	0.5*	1.2
Mn	4.9	2.2	2.0	1.7	1.6

-140+125 M

Cu	1.8*	3.7	3.5	3.6	6.3
Pb	41.3	19.3	10.2	11.9	6.9
Zn	12.5	7.7	8.9	8.4	3.7
Fe	1.4	1.1	0.8	0.9	1.0
Mn	7.7	3.9	3.8	1.6	2.3

-140 M

Cu	10.6	4.8	2.1*	4.6	1.2*
Pb	33.2	17.9	4.6	8.5	6.2
Zn	7.5	2.3	3.6	4.3	3.9
Fe	1.9	1.3	0.8	0.5*	1.1
Mn	3.3	3.8	1.2*	2.2	1.2*

-190+140 M

Cu	10.4	10.1	10.3	2.5	5.4
Pb	56.1	18.4	19.3	15.9	14.4
Zn	17.7	2.1	3.2	8.2	4.9
Fe	2.3	0.8	1.3	1.1	0.8*
Mn	5.6	6.0	3.6	0.9*	2.2

TABLE 2.9 continued ...

TABLE 2.9 continued ...

-190 M

	0.05g	0.1g	0.2g	0.3g	0.5g
Cu	4.0	5.1	4.9	2.0*	ND
Pb	32.4	10.8	6.4	5.8	ND
Zn	6.1	3.5	3.9	10.6	ND
Fe	1.0	1.4	1.0	2.9	ND
Mn	4.5	1.3*	1.1*	3.9	ND

-190 T

Cu	4.1	4.3	4.5	2.7	4.0
Pb	34.1	7.4	7.6	3.9*	8.6
Zn	9.4	5.0	4.7	8.0	12.7
Fe	1.4	0.3*	1.2	0.9	0.9
Mn	2.6	4.9	1.8	1.8	5.9

M denotes separation by Micropanner

T denotes separation by Tetrabromoethane

\* denotes precision level significantly low

ND denotes not determined

N = 5

TABLE 2.10

Site B, light mineral separates.  
Means of precision estimates for each set of conditions.

## -70 micron M

	0.05g	0.1g	0.2g	0.3g	0.5g
Cu	5.6	4.3	0.9*	1.3*	2.1
Pb	7.4	4.4*	3.7*	2.4*	1.6*
Zn	5.6	2.4	1.0	1.3	1.7
Fe	2.1	0.9	0.3*	0.5	0.4*
Mn	4.6	2.4	0.8*	1.1*	1.5

## -125+70 M

Cu	3.1	1.6	2.8	3.2	1.9
Pb	4.4*	0.0*	2.9*	5.5*	2.5*
Zn	3.2	0.9	2.2	3.1	1.7
Fe	1.2	0.4*	1.2	1.4	0.8
Mn	1.8	1.7	1.7	2.9	2.2

## -125 M

Cu	2.2	2.2	1.6	2.8	0.4*
Pb	3.2*	3.2*	1.8*	2.6*	1.5*
Zn	1.9	1.8	1.7	1.6	1.0
Fe	1.0	0.6	0.8	1.2	0.3*
Mn	1.4	1.8	1.3	2.3	0.6*

## -140+125 M

Cu	4.4	2.4	3.5	2.8	3.3
Pb	9.0	8.3	5.8	6.4	2.7*
Zn	3.1	2.8	3.4	2.0	2.5
Fe	1.0	1.0	0.9	0.9	1.2
Mn	4.5	3.1	2.5	1.3	2.4

## -140 M

Cu	4.0	0.6*	0.8*	2.3	1.9
Pb	14.1	2.3*	13.7	1.3*	3.1*
Zn	1.2	0.6*	1.9	2.7	1.9
Fe	1.0	0.7	1.8	0.9	0.4*
Mn	2.3	0.6*	0.5*	2.1	0.7*

## -190+140 M

Cu	7.0	5.3	3.9	4.5	2.0
Pb	14.5	18.7	6.9	5.6	7.2
Zn	3.5	3.1	3.5	3.3	2.8
Fe	1.6	0.9	1.2	1.5	1.8
Mn	2.8	2.5	3.6	2.9	3.0

TABLE 2.10 continued ...



TABLE 2.10 continued ...

-190 M

	0.05g	0.1g	0.2g	0.3g	0.5g
Cu	2.8	4.5	2.5	2.5	1.5
Pb	10.4	6.8	8.4	2.7*	2.2*
Zn	3.1	3.9	0.9	1.8	1.8
Fe	0.4*	1.5	0.4*	0.9	1.3
Mn	1.2	3.8	1.6	1.6	1.3

-190 T

Cu	3.6	2.8	2.1	3.3	1.6
Pb	9.8	3.0*	3.2*	2.3*	2.9*
Zn	2.1	3.1	1.1*	2.0	0.9*
Fe	1.5	0.9	0.4*	1.3	0.6
Mn	2.3	2.0	1.2	1.2	0.9*

M denotes separation by Micropanner

T denotes separation by Tetrabromeothane

\* denotes precision level significantly low

N = 5

TABLE 2.11

Site G heavy mineral separates  
Means of precision estimates for each set of conditions.

## -70 micron M

	0.05g	0.1g	0.2g	0.3g	0.5g
Cu	2.2	1.2	1.1*	2.5	1.3
Pb	1.4	0.5*	0.6*	1.9	1.8
Zn	1.8	0.9*	1.4	2.3	0.8*
Fe	0.9	0.7	0.9	1.7	1.0
Mn	2.8	1.2	1.0*	2.6	0.9*

## -125+70 M

Cu	1.0*	0.7*	2.9	2.5	1.8
Pb	1.8	1.0	1.1	1.9	1.4
Zn	2.6	4.6	1.3	1.6	2.1
Fe	0.6	1.0	0.8	1.3	0.4*
Mn	3.1	1.5	1.2	2.2	1.1

## -125 M

Cu	1.3	1.6	2.0	2.7	2.9
Pb	2.1	0.6*	0.9	2.0	1.8
Zn	4.0	2.6	4.3	3.6	1.5
Fe	0.7	0.7	1.3	1.9	1.1
Mn	2.8	1.5	1.5	3.8	2.8

## -140+125 M

Cu	2.0	1.9	1.5	2.7	2.9
Pb	2.8	1.5	1.2	1.9	1.5
Zn	8.5	6.7	3.9	3.4	1.7
Fe	0.4*	0.7	1.2	1.0	1.3
Mn	4.0	1.1	2.2	2.4	1.8

## -140 M

Cu	1.0*	2.4	2.5	1.3	0.1*
Pb	1.4	1.2	1.8	1.3	0.7*
Zn	2.2	3.1	2.2	4.3	1.7
Fe	0.7	0.8	1.4	0.8	0.5*
Mn	1.2	2.6	2.4	1.0*	0.9*

## -190+140 M

Cu	7.2	6.8	3.8	2.3	2.3
Pb	3.5	2.0	1.7	1.4	2.0
Zn	16.1	9.9	5.4	6.8	4.8
Fe	1.4	0.9	1.1	0.8	0.9
Mn	13.5	4.7	3.6	2.8	3.9

TABLE 2.11 continued ...

TABLE 2.11 continued ...

-190+140 T

	0.05g	0.1g	0.2g	0.3g	0.5g
Cu	4.7	5.5	2.6	2.7	2.7
Pb	2.9	2.3	2.3	1.2	1.5
Zn	10.4	7.2	6.4	4.9	5.0
Fe	1.5	1.0	1.0	0.6	1.6
Mn	5.8	3.0	2.8	1.7	2.8

-190 T

Cu	4.2	2.6	1.9	0.6*	1.3
Pb	1.3	0.6*	1.9	0.9	1.0
Zn	7.7	12.7	2.4	2.6	1.2
Fe	1.1	1.1	1.8	0.5*	1.2
Mn	4.7	2.2	3.3	2.5	1.4

-660+190 T

Cu	10.3	14.4	7.3	7.0	9.3
Pb	5.9	3.9	4.2	3.7	1.7
Zn	19.8	9.8	8.5	15.6	4.7
Fe	1.9	2.1	1.0	1.6	0.9
Mn	9.6	9.2	3.9	5.3	2.1

M denotes separation by Micropanner

T denotes separation by Tetrabromoethane

\* denotes precision level significantly low

N = 5.

TABLE 2.12

Site G light mineral separates.  
Means of precision estimates for each set of conditions.

## -70 micron M

	0.05g	0.1g	0.2g	0.3g	0.5g
Cu	0.6*	0.7*	0.7*	1.3	1.7
Pb	0.9	1.0	0.7*	1.2	1.1
Zn	0.8*	1.7	1.6	2.0	1.1*
Fe	0.3*	1.1	0.6	1.4	1.2
Mn	0.3*	1.3	0.9*	1.3	2.0

## -125+70 M

Cu	2.9	3.0	1.4	1.6	0.7*
Pb	2.5	3.4	1.0	1.3	1.4
Zn	1.7	2.8	2.1	3.0	1.7
Fe	1.4	2.5	0.6	0.9	0.6
Mn	2.3	3.6	2.1	1.8	0.5*

## -125 M

Cu	1.6	1.8	0.9*	2.6	ND
Pb	1.3	1.1	0.7*	2.7	ND
Zn	1.4	3.4	0.5*	3.0	ND
Fe	0.7	1.3	0.6	2.6	ND
Mn	1.6	1.5	1.4	2.5	ND

## -140+125 M

Cu	3.1	2.2	2.8	1.6	1.6
Pb	1.5	1.3	1.9	1.1	0.8
Zn	8.4	1.8	3.3	3.0	1.5
Fe	1.4	1.4	1.2	0.5*	0.7
Mn	1.8	4.0	2.2	1.6	0.3*

## -140 M

Cu	1.2	1.6	2.3	2.1	0.9*
Pb	0.7*	1.2	1.2	1.1	0.7*
Zn	1.5	1.4	1.7	1.7	1.6
Fe	0.5*	1.2	2.0	1.0	0.2*
Mn	1.4	1.1	1.8	1.9	1.8

## -190+140 M

Cu	3.0	2.7	1.0	3.5	1.5
Pb	1.8	0.8	1.3	1.2	1.6
Zn	8.7	4.3	5.3	4.8	2.8
Fe	1.7	0.6	1.6	1.5	0.5*
Mn	2.1	2.5	2.4	1.8	1.6

TABLE 2.12 continued ...

TABLE 2.12 continued ...

-190 + 140 T

	0.05g	0.1g	0.2g	0.3g	0.5g
Cu	1.4	2.2	1.2	2.0	2.6
Pb	1.9	0.8	0.9	2.0	0.8
Zn	4.7	1.6	2.8	4.3	1.5
Fe	1.8	0.9	0.9	0.4*	1.4
Mn	2.4	2.3	2.0	2.4	1.7

-190 T

Cu	3.9	2.6	1.6	1.8	1.7
Pb	2.7	1.8	1.1	1.3	1.7
Zn	2.5	2.5	2.3	3.0	2.6
Fe	2.5	1.1	0.7	1.2	1.5
Mn	1.8	1.3	1.2	0.8*	1.4

-660+190 T

Cu	12.4	2.8	7.0	3.9	5.8
Pb	3.7	1.9	3.0	1.4	1.7
Zn	29.4	4.3	21.6	8.4	11.5
Fe	8.1	2.5	2.2	1.8	2.5
Mn	15.0	7.5	5.6	5.9	3.4

M denotes separation with the Micropanner

T denotes separation with Tetrabromoethane

ND denotes Not Determined

N = 5

\* denotes precision level significantly low

TABLE 2.13 Numbers of re-reading pairs considered for each element.

	Cu	Pb	Zn	Fe	Mn
Site B	72	80	97	0	0
Site G	78	55	80	90	79
Site Y	<u>80</u>	<u>77</u>	<u>82</u>	<u>83</u>	<u>78</u>
Total	230	212	259	173	157

The distribution of the precision values, calculated by TOMHOW for each re-reading pair, should centre on zero, since if the instrument is in perfect adjustment, each re-read value should be the same as the original. Thus, in the present study, if an original,  $x_1$ , is smaller than its duplicate,  $x_2$ , a negative value has been ascribed to the precision.

A sample whose metal content causes it to be very low on the instrument scale will be more prone to re-reading error than a sample which is read higher up the scale. Therefore, it is logical to distribute the errors according to concentration, and it can be seen from Table 2.14 that the errors are generally greatest at low concentration.

Table 2.14 tabulates the distribution of precision estimates from re-reading pairs and, in the final column, gives an upper limit of mean plus one standard deviation to the precision attributable to re-reading error. This limit of  $\bar{P} + S.D.$  was chosen at a particularly low level so as to exclude, as still subject to sub-sampling error, most precision values from the main experiment about which some doubt remains. Thus, for the results from a particular combination of particle size and quantity to be considered free from sub-sampling error, its precision value must lie within one standard deviation of the mean re-reading precision at that concentration. All values which fulfil these conditions are denoted with an asterisk in Tables 2.4, 2.5, 2.6, 2.9, 2.10, 2.11 and 2.12.

Table 2.15 shows a break-down of the numbers of significant combinations for sites B, G and Y taken from the data of Tables 2.4, 2.5 and 2.6. It is immediately apparent that the results for fractions lying between two mesh sizes (i.e. -660+190 micron etc.) are generally

poor. Even the minus 125+70 micron fraction has only 44.0% of its total possible sample size/element combinations free from sub-sampling errors, and for all the other such fractions this total figure falls below 15%. This is indeed as one would expect when dealing with elements which are concentrated in the finest sized particles, (see Table 2.1).

In considering the other mesh fractions, (-660, -190, -140, -125 and -70 micron), the results from site G are perhaps the most informative, since the metal values for this site are very high, and therefore less prone to re-reading errors. From the site G results, it is clear that only in the minus 125 micron and minus 70 micron fractions do the majority of the results show insignificant sub-sampling errors. Since there is little to choose between these two fractions, obviously the coarser one is preferable from a practical point of view, meaning smaller samples may be collected in the field. The results for the other two sites demonstrate the same point a little less forcibly, and, in the light of this discussion, the minus 125 micron fraction was selected as the optimum for further work. It is worth noting that the minus 190 micron fraction, so commonly used in exploration work has, overall, only 32% of its possible sample weight/element combinations free from sub-sampling errors, almost half the number for the minus 125 micron fraction, and at site G it comes out particularly poorly, with only 3% significant combinations.

Turning now to the problem of sample weight, combinations of the relevant results from Tables 2.4, 2.5 and 2.6 are to be found in Table 2.16.

TABLE 2.14

Distribution of re-reading error precision.

Element	Range (ppm)	N	$\bar{P}$	SD	$\bar{P} + SD$
Cu	0- 30	67	0.28	8.38	8.66
	31- 60	22	0.73	1.46	2.19
	60- 100	62	0.09	1.23	1.32
	251- 500	51	0.22	0.74	0.96
	501-1000	28	0.26	0.91	1.17
Pb	0- 30	19	4.51	15.90	20.41
	31- 60	77	0.49	3.78	4.27
	61- 150	61	1.78	3.91	5.69
	2000-4000	29	0.22	0.56	0.78
	4000+	26	0.32	0.46	0.78
Zn	0- 30	11	-0.20	0.66	0.46
	31- 60	20	0.44	1.08	1.52
	61- 100	65	0.40	1.24	1.64
	101- 150	69	0.34	1.27	1.61
	151- 250	17	-0.08	0.93	0.85
	251- 500	43	0.17	0.94	1.11
	500+	34	0.20	0.77	0.97
Fe	0-10,000	30	0.16	0.66	0.83
	10,001-20,000	53	-0.11	0.56	0.45
	20,001-30,000	23	-0.05	0.45	0.40
	30,001-50,000	59	0.14	0.39	0.53
	50,001+	8	0.16	0.29	0.45
Mn	100- 150	17	2.54	4.66	7.20
	151- 250	8	0.51	0.84	1.35
	251- 500	47	0.20	0.98	1.19
	501- 750	62	0.25	0.67	0.92
	751+	23	0.40	0.66	1.06

Where N is the number of observations within a particular range.

 $\bar{P}$  is the mean precision within a range.SD is the standard deviation of precisions about  $\bar{P}$ .



TABLE 2.15

Percentages of sample weight/element combinations of significantly low precision for each mesh fraction, unseparated samples.

<u>Mesh fraction</u> <u>(microns)</u>	<u>Site B</u> <u>(%)</u>	<u>Site G</u> <u>(%)</u>	<u>Site Y</u> <u>(%)</u>	<u>Overall</u> <u>(%)</u>
-70	50	67	60	59
-125+70	42	47	43	44
-125	50	70	67	62
-140+125	25	7	13	15
-140	58	20	63	47
-190+140	21	0	17	13
-190	42	3	50	32
-660+190	21	0	17	13
-660	8	0	20	9
-2000+660	13	0	13	9
Totals:	33	21	36	

TABLE 2.16

Percentages of element/sample site combinations of significantly low precision for each sample weight at minus 125 micron, and overall.

<u>Sample weight (g)</u>	<u>% significant</u> <u>combinations</u> <u>at -125 micron</u>	<u>% significant</u> <u>combinations overall</u>
0.05	57	15
0.1	64	26
0.2	64	29
0.3	71	35
0.5	79	40
1.0	43	35

Thus, it can be seen that the best results are obtained from the analysis of 0.5g sample weights, which is well within the practical limits set by the use of standard laboratory test tubes.

#### 2.3.3.2. Unseparated samples for Sn

Analysis of all samples from sites O and P for Sn at this time was conducted according to the method described by Stanton (1966, p. 81). Analytical difficulties, to be discussed more completely in Chapter 5, are responsible for the incomplete data in Table 2.8, and leave the validity of the results for both sites questionable, due to the probable introduction of variable analytical precision.

However, it is worth noting that the data appears to show that the best precision is obtained by the use of minus 190 micron material, especially for site P. This observation was confirmed by re-analysing 0.5g sample weights of the minus 660, minus 190, minus 140, minus 125 and minus 70 micron fractions of site P with the samples read in random, not systematic, order. Precisions of 7.6%, 3.0%, 9.1%, 7.0% and 4.9% were obtained for the minus 660, minus 190, minus 140, minus 125 and minus 70 micron fractions respectively, confirming the precision minimum at minus 190 microns.

#### 2.3.3.3. Heavy and light mineral separates.

The significance of the precision values calculated from the heavy and light mineral separates was assessed as described in Section 2.3.3.1 (p. 2.11) and the percentages of significantly low precision estimates are tabulated in Table 2.17. Comparison with Table 2.15 shows that no improvement in precision is to be gained from the use of heavy mineral separation prior to analysis, in fact, the contrary seems to be true. It appears that a distinct loss in precision

TABLE 2.17

Percentages of sample weight/element combinations of significantly low precision for each mesh fraction, separated and unseparated portions.

Mesh fraction (microns)	H	Site G		H	Site B		Overall	
		L	U		L	U	Sep.	U
-70(M)	28	36	67	24	40	50	32	59
-125+70(M)	12	8	47	0	24	42	11	44
-125(M)	5	15	70	12	32	50	17	62
-140+125(M)	4	8	7	4	4	25	5	15
-140(M)	24	20	20	20	40	58	26	47
-190+140(M)	0	4	0	8	0	21	3	13
-190(T)	12	4	3	8	32	42	14	32
-660+190(T)	0	0	0	ND	ND	21	ND	13
Totals	11	12	21	9	25	33		

M denotes separation by Micropanner  
 T denotes separation by tetrabromoethane  
 ND denotes Not Determined  
 H denotes heavy mineral separate  
 L denotes light mineral separate  
 U denotes unseparated  
 Sep. denotes overall for both separated portions.

is experienced, mesh fraction for mesh fraction, when the samples are split before analysis.

#### 2.3.4 Conclusions

The first part of this experiment was concerned with the optimisation of sample weight and mesh fraction taken for analysis of metals commonly concentrated in the finest particle sizes of a stream sediment. Precision values, calculated from replicate analyses of various weights of various mesh fractions, were assessed in terms of levels which can be accounted for solely in terms of instrumental (re-reading) errors. This has led to the selection of 0.5g of minus 125 micron material as an optimum combination.

Table 2.18 illustrates the percentage of minus 125 micron material present in the five bulk samples studied in this experiment, and the average, in excess of 2.5% would result in at least 25g of minus 125 micron material being available from a 1kg sample.

TABLE 2.18

	<u>Site B</u>	<u>Site G</u>	<u>Site O</u>	<u>Site P</u>	<u>Site Y</u>
Total Sample weight (g)	31225	38820	50420	49580	40310
Weight - 125 micron (g)	1113	1773	168	1343	1000
% - 125 micron	3.56	4.57	0.43	2.71	2.48

This conclusion is drawn from data from only three localities, but similar chemical processes controlling secondary dispersion in the surface environment, might perhaps be presumed to prevail in other areas, at least in temperate latitudes, and it therefore seems reasonable to propose that this optimum combination may have wider application than the restricted field area chosen for this study.

The extension of this experiment into elements dispersed clastically in the surface environment was complicated by analytical problems. Notwithstanding, sufficient data is available in Table 2.7 and, more particularly in Table 2.8, to suggest that the minus 190 micron fraction may be preferable when dealing with tin. However, clastic dispersion of elements is dependent upon the physical properties of the minerals concerned, and it would be unlikely, for example, that cassiterite and wolframite would disintegrate into similar sized grains even in the same stream. In addition, it appears logical to assume that grains of cassiterite, for example, introduced into a stream, will progressively abrade to smaller sizes the further they are transported, subject to a final limiting size. Therefore, it is possible that the conclusion concerning the suitability of minus 190 micron material from site P may in part be a function of

distance downstream from the cassiterite source, and therefore of only local significance.

Separating samples into heavy and light mineral portions has not proved to be worthwhile in terms of the analytical precisions obtained for most elements. Thus the precision levels for Cu, Pb, Zn, Fe and Mn are generally worse than for unseparated samples. However, for some elements, such as Sn and W, which are probably dispersed as clastic mineral grains, this practice may be more worthwhile.

The differing hydrodynamic properties of particles within samples of wide-ranging grain size brings the usefulness of a mechanical separator, such as the Micropanner, into serious doubt.

## CHAPTER 3

### THE IMPORTANCE OF SAMPLING VARIABILITY AND SOME FACTORS WHICH INFLUENCE IT

#### 3.1. INTRODUCTION

#### 3.2. EXAMINATION OF SOURCES OF VARIANCE IN A FIELD SITUATION

##### 3.2.1. Introduction

##### 3.2.2. Partition of variance

###### 3.2.2.1. Theory

###### 3.2.2.2. Total data variance

###### 3.2.2.3. Within site variance

##### 3.2.3. Comparision with a previous survey

###### 3.2.3.1. Introduction

###### 3.2.3.2. Total data variance

###### 3.2.3.3. Total error variance

###### 3.2.3.4. Partition of error variance

#### 3.3. EXAMINATION OF SAMPLING PROCEDURE

##### 3.3.1. Introduction

##### 3.3.2. Dependence of sampling error upon iron precipitation

##### 3.3.3. Dependence of sampling error upon depth of sampling, and number of "grabs" of sediment taken.

#### 3.4. EXAMINATION OF VARIABLE SAMPLING PRECISION

#### 3.5 CONCLUSIONS

CHAPTER 3THE IMPORTANCE OF SAMPLING VARIABILITY AND SOME FACTORS WHICH INFLUENCE IT3.1 INTRODUCTION

The exploration geologist when sampling stream sediment, collects a small bag of material, usually less than a kilogram wet-weight, in the expectation that this sample will be representative of the geochemistry of the stream's entire catchment area above the sampling point. It has long been realised that these assumptions are far from justified. Nevertheless, although it is impossible to assess the degree to which the stream sediment is representative of the catchment area bedrock geochemistry, it is possible to make some assessment of the degree to which the sample represents the whole sediment load at that point.

Many authors have reported on methods of monitoring sampling errors in geochemistry. Miesch (1967) and Baird et al (1967), amongst many others, dealt with the problems of rock-mass sampling, and more recently attention was turned onto the problems of sediment sample representativity by such writers as Miesch (1971), Plant (1971), Howarth and Lowenstein (1971), Bolviken and Sinding-Larsen (1973) and Plant et al (1975). These authors agreed on the use of replicate sample collections as a means of determining total error variance.

Data is presented here, from a detailed survey of Yarner Wood, near Bovey Tracey in South Devon (see Fig. 1.2.) from which errors attributable to sampling, sub-sampling and analysis can be isolated. Various factors concerned with the secondary dispersion environment were examined as possible sources of some of the sampling error, and the effects on analytical error of the optimum techniques devised in Chapter 2, were examined by reference to work done in the same area by Harrison (1974).

Plant (1971) mentioned the effects which oxidation potential (Eh) and, to a lesser extent, acidity, (pH), have on the metal concentration in a sediment sample, especially of Fe, Mn and related elements, and recommended that samples should be collected from below the water-sediment interface. A sampling programme, designed to investigate some of the possible effects of this procedure, produced somewhat spectacular results which highlight the necessity of further investigating this technique.

The number of handfuls, or grabs, of sediment necessary to produce a representative sample was also investigated, but the results are probably affected by the depth of collection just described and are therefore not conclusive.

A further collection of samples was made in the River Mardle near Brookwood and was used as a method of testing for the presence of variable sampling precision as defined by Miesch (1967), (see Fig. 1.3).

### 3.2. EXAMINATION OF SOURCES OF VARIANCE IN A FIELD SITUATION

#### 3.2.1. Introduction

Yarner Wood, near Bovey Tracey, S. Devon, was chosen as a field area within which to test methods of assessing and reducing errors, (see Fig. 1.1). Yarner Stream has a total length of approximately 3 km and with its tributary, the Woodcock Stream, drains an area of approximately 4 km<sup>2</sup> (see Fig. 1.2). It flows entirely over the metamorphosed Carboniferous sediments known locally as Killas, and drains the site of the Devon Wheal Frances mine which produced 2300 tons of copper ore between 1858 to 1865. (Nature Conservancy Council, 1971). A further factor influencing the choice of this area was that the upper 1.8 km of the Yarner Stream lie within the Yarner Wood National Nature Reserve, and are therefore subject to only minimal recent human disturbance.



Chapter 8 deals with the significance of the detailed results from the area. Within this area eighty-eight sites were sampled, of which fifty were sampled in duplicate, whilst more than fifty samples were analysed in duplicate for nine elements, and numerous duplicate analyses of the same digestion were also completed.

### 3.2.2. Partition of variance

#### 3.2.2.1 Theory.

Garrett (1969 and 1973) outlines a now widely used method for the estimation of combined sampling and analytical variance from the analysis of replicate samples as:-

$$S_{SA}^2 = \frac{1}{N} \sum_{i=1}^N \frac{1}{n-1} \sum_{j=1}^n (x_j - \bar{x})^2 \quad (3.1)$$

where  $S_{SA}^2$  is combined sampling and analytical variance.

$N$  is the number of replicated sites.

$n$  is the number of replications per site.

$x_j$  is the logarithm of the concentration of metal in the  $j$ th sample at the  $i$ th site.

$\bar{x}$  is the logarithm of the mean concentration of the  $j$  samples at the  $i$ th site.

Where  $n = 2$ , this reduces to:-

$$S_{SA}^2 = \frac{1}{2N} \sum_{i=1}^N (x_{1i} - x_{2i})^2 \quad (3.2)$$

where  $x_{1i}$  is the logarithm of the routine value at site  $i$ .

$x_{2i}$  is the logarithm of the duplicate at site  $i$ .

The variance,  $S_{SA}^2$ , may be redefined as the total error variance,  $S_{TE}^2$ , as it represents variance introduced via errors in sampling procedure,

sub-sampling procedure and analytical procedure, and therefore, since variance is an additive quantity, it may be said, by analogy with Volborth (1969, p.36), that:-

$$S_{TE}^2 = S_S^2 + S_{SS}^2 + S_A^2 \quad (3.3)$$

where  $S_{TE}^2$  is total error variance,

$S_S^2$  is variance due to sampling error.

$S_{SS}^2$  is variance due to sub-sampling error, and

$S_A^2$  is variance due to analytical error.

If a number of samples are sub-sampled twice, i.e. two portions of material from the same sample are subjected to independent analysis, we may estimate the combined sub-sampling and analytical variance,

$S_{SS+A}^2$ , as

$$S_{SS+A}^2 = \frac{1}{2M} \sum_{i=1}^M (x_{1i} - x_{2i})^2 \quad (3.4)$$

where  $M$  is the number of duplicated samples.

$x_{1i}$  is the logarithm of the routine value for duplication  $i$ ,

and  $x_{2i}$  is the logarithm of the duplicate value for duplication  $i$ .

Similarly, if  $L$  sample leaches are analysed twice by whatever analytical method is in use, the instrumental or re-read variance, often simply referred to as analytical variance,  $S_A^2$ , may be estimated as:-

$$S_A^2 = \frac{1}{2L} \sum_{i=1}^L (x_{1i} - x_{2i})^2 \quad (3.5)$$

where  $x_{1i}$  is the logarithm of the routine reading,

and  $x_{2i}$  is the logarithm of the repeat reading.

Thus, the variances due to the individual effects of sampling,  $S_S^2$ , sub-sampling,  $S_{SS}^2$ , and analysis,  $S_A^2$ , can be estimated, since

$S_A^2$  is derived directly as above,

$$S_{SS}^2 = S_{SS+A}^2 - S_A^2, \quad (3.6)$$

$$\text{and } S_S^2 = S_{TE}^2 - S_{SS+A}^2. \quad (3.7)$$

Therefore the relative importance of the various components of the total error may be assessed, and where necessary attempts may be made to reduce components which are abnormally high.

#### 3.2.2.2. Total data variance.

Garrett (1973) points out the necessity for the variance of the routine samples from each replication site (i.e.  $x_{1i}$  in Equation (3.2) in the case of duplicate samples) to be comparable with the variance of the entire set of sample sites in order for the estimates of error from the duplicates to be significant. In the case of the present study,  $T = 88$  localities were sampled, and duplicates were collected at  $N = 50$  of them. Thus it is necessary that  $S_{TD}^2$  should be comparable with  $S_D^2$ , where:-

$$S_{TD}^2 = \frac{1}{T-1} \sum_{i=1}^T (x_i - \bar{x})^2 \quad (3.8)$$

$S_{TD}^2$  is the Total Data variance.

$T$  is the total number of localities sampled.

$x_i$  is the logarithm of the routine sample at the  $i$ th site.

$\bar{x}$  is the logarithm of the overall mean of the  $T$  routine samples,

and 
$$S_D^2 = \frac{1}{N-1} \sum_{i=1}^N (x_i - \bar{x}_D)^2 \quad (3.9)$$

$S_D^2$  is the variance of routine samples at duplicated localities.

$N$  is the number of localities duplicated.

$x_i$  is the logarithm of the routine sample at the  $i$ th locality

$\bar{x}_D$  is the logarithm of the mean of the routine samples from the  $N$  duplicated localities.

The calculated variances are tabulated, along with F ratio values and critical values of F, for all nine elements in Table 3.1

TABLE 3.1

Comparison of overall data variance with variance between replicated sites, via Snedecor's F test.

	$S^2_{TD}$	$S^2_D$	F	$F_c$
Cu	0.0966	0.1352	1.40	1.51
Pb	0.0695	0.0584	1.19	1.55
Zn	0.1717	0.1847	1.08	1.51
Fe	0.1258	0.0992	1.27	1.55
Mn	0.3191	0.3311	1.04	1.51
As	0.2781	0.2369	1.17	1.55
Cd	0.0619	0.0595	1.04	1.55
Co	0.1036	0.0693	1.49	1.55
Ni	0.1021	0.1230	1.20	1.51

In each case  $T = 88$

$N = 50$

$F_c$  denotes critical value of F at  $\alpha = 0.05$ .

It can be seen that in each case the total data variance and the duplicated sites total variance are comparable at the 95% confidence level, thus fulfilling the first of Garrett's (1973) prerequisites.

#### 3.2.2.3. Within site variance.

In order that the results of a geochemical investigation may be considered significant, it is necessary that the total error variance,  $S^2_{TE}$ , should be significantly less than the total variance at duplicated sites,  $S^2_D$ , i.e. between sites variance must be greater than within sites

variance. Values of  $S_{TE}^2$ , calculated from Equation (3.3), and  $S_D^2$ , calculated from Equation (3.9), are given in Table 3.2 for all nine elements.

TABLE 3.2

Comparison of total data variance with total error variance, via Snedecor's F test.

	$S_D^2$	$S_{TE}^2$	$F = S_D^2 / S_{TE}^2$	$F_c$
Cu	0.1352	$1.77 \times 10^{-3}$	76.4	1.61
Pb	0.0584	$1.60 \times 10^{-3}$	36.4	1.61
Zn	0.1847	$3.19 \times 10^{-3}$	57.9	1.61
Fe	0.0992	$3.64 \times 10^{-3}$	27.3	1.61
Mn	0.3311	$1.50 \times 10^{-2}$	22.1	1.61
As	0.2369	$3.89 \times 10^{-3}$	60.9	1.61
Cd	0.0595	$4.21 \times 10^{-3}$	14.1	1.61
Co	0.0693	$4.84 \times 10^{-3}$	14.3	1.61
Ni	0.1230	$3.32 \times 10^{-3}$	37.1	1.61

N = 50 throughout

$F_c$  denotes critical F ratio at  $\alpha = 0.05$

In each case it can be seen that the total error variation is many times smaller than the total variation at duplicated sites and interpretation of the results may thus proceed.

It is now possible, using Equations (3.5), (3.6) and (3.7) to split up the total error variance,  $S_{TE}^2$ , into its constituent components. These results are shown in Table 3.3, and firstly mention must be made of the results for Cd, where the combined sub-sampling and analytical errors are greater than the total error. This reflects the fact that the Cd values reported from the samples in question were nearly all very low

and thus close to the detection limit of the instrument, which in turn means that a small difference in readings on the instrument produces a very significant discrepancy between calculated Cd concentrations.

This fact is reflected in the absolute level of analytical variance,  $S_A^2$ , quoted for Cd, which is 6.5 times greater than the analytical variance for any other element. A similar problem was encountered for one pair of readings for As, where the level of concentration was very low, but since this was the only pair at such a low level, it was omitted from the calculation of total and of combined analytical and sub-sampling variance.

From Table 3.3 it can be seen that for all eight elements, (excluding Cd) sampling error is by far the major constituent. It is most prominent, not only as a proportion, but also in absolute terms, for Mn, which supports the idea of rapid fluctuations in Eh and pH conditions as suggested in Section 3.1, (p. 3.2).

This approach, partitioning error into its constituent components, is useful because, for example, it has highlighted the problems concerning Cd, and will lead to the interpretation for that element being of only a qualitative nature. It also throws light upon areas where improvements in technique might be concentrated, for example, on reducing sub-sampling errors for Cu, Fe and Ni, and also on reducing analytical errors for Cd, Ni and, possibly, Zn.

The ability to proportion error variance into its constituent components has, in this instance, clearly demonstrated that for most elements under consideration the majority of error is introduced via sampling techniques. Future attempts to substantially reduce total error variance ought not to ignore this aspect of procedure.

TABLE 3.3

Partition of total error variance into its component parts

Element	$S^2_{TE}$	$S^2_{ss+A}$	$S^2_A$	Proportion Analytical Error	$S^2_{ss}$	Proportion Sub-sampling Error	$S^2_s$	Proportion Sampling Error
Cu	$1.77 \times 10^{-3}$	$5.46 \times 10^{-4}$	$1.49 \times 10^{-4}$	8.4%	$3.97 \times 10^{-4}$	22.4%	$1.22 \times 10^{-3}$	69.1%
Pb	$1.60 \times 10^{-3}$	$2.32 \times 10^{-4}$	$1.55 \times 10^{-4}$	9.7%	$7.95 \times 10^{-5}$	4.9%	$1.37 \times 10^{-3}$	85.5%
Zn	$3.19 \times 10^{-3}$	$5.74 \times 10^{-4}$	$3.55 \times 10^{-4}$	11.1%	$2.19 \times 10^{-4}$	6.9%	$2.62 \times 10^{-3}$	82.0%
Fe	$3.64 \times 10^{-3}$	$1.05 \times 10^{-3}$	$2.21 \times 10^{-4}$	6.1%	$8.31 \times 10^{-4}$	22.9%	$2.58 \times 10^{-3}$	71.0%
Mn	$1.50 \times 10^{-2}$	$9.37 \times 10^{-4}$	$1.01 \times 10^{-4}$	0.7%	$8.36 \times 10^{-4}$	5.6%	$1.41 \times 10^{-2}$	93.8%
As	$3.89 \times 10^{-3}$	$3.31 \times 10^{-4}$	$2.87 \times 10^{-4}$	7.4%	$4.41 \times 10^{-5}$	1.1%	$3.56 \times 10^{-3}$	91.5%
Cd	$4.21 \times 10^{-3}$	$4.25 \times 10^{-3}$	$3.64 \times 10^{-3}$	86.5%	$6.11 \times 10^{-4}$	14.5%	ND	ND
Co	$4.84 \times 10^{-3}$	$6.16 \times 10^{-4}$	$1.65 \times 10^{-4}$	3.4%	$4.51 \times 10^{-4}$	9.3%	$4.22 \times 10^{-3}$	87.3%
Ni	$3.32 \times 10^{-3}$	$1.42 \times 10^{-3}$	$5.60 \times 10^{-4}$	16.9%	$8.56 \times 10^{-4}$	25.8%	$1.90 \times 10^{-3}$	57.3%

ND denotes no determination possible because combined analytical and sub-sampling variance is larger than total error variance.

The above is all additional to the information which would have been available had only total error variance been calculated, in which case the only significant point would have been the higher absolute variance value for Mn, and even then the fact that this is caused largely by sampling error would have been missed.

### 3.2.3. Comparison with a previous survey

#### 3.2.3.1. Introduction.

Harrison (1974) reported on a detailed stream sediment survey of the Yarner Stream during which samples were analysed for Cu, Pb, Zn, Fe and Mn. Duplicate analyses, 24 pairs all told, are quoted, and duplicate sampling, as a means of assessing total error variance, was carried out. Although the results from the 45 duplicate samples are given, it has proved impossible to determine where the routine samples were collected from. Therefore it was necessary to re-calculate the total data variance at duplicated sites, and to work back to the total error variance, via the F ratios.

#### 3.2.3.2. Total data variance.

The total data variance from duplication sites,  $S_{D(H)}^2$ , has been calculated from Harrison's figures, and compared with the corresponding values from the present study,  $S_{D(R)}^2$ . Table 3.4 shows these figures and the relevant F test ratios.

From Table 3.4 it can be seen that the two sets of total data variance at duplication sites are comparable for Cu, Pb, Fe and Mn, and indeed at the 99% confidence level the critical F value is 2.03, thus making the Zn values comparable. The apparent discrepancy in the Zn values at the lower confidence level may be explained by the fact that the right bank tributary which joins Yarner Stream at 27790784, is the source of a major Zn anomaly. It was sampled in detail during the present



TABLE 3.4

Total data variance at duplication sites from previous and present studies.

Element	$S^2_{D(H)}$	$S^2_{D(R)}$	F	$F_c$
Cu	0.134	0.135	1.01	1.65
Pb	0.084	0.058	1.45	1.65
Zn	0.094	0.185	1.97	1.65
Fe	0.120	0.099	1.21	1.65
Mn	0.341	0.331	1.03	1.65

$F_c$  denotes Critical F ratio at  $\alpha = 0.05$

study, but was not during Harrison's project, and therefore, the high Zn values obtained from samples in this tributary will increase  $S^2_{D(R)}$  accordingly.

#### 3.2.3.3. Total error variance.

Total error variance from the present study,  $S^2_{TE(R)}$ , is given in Table 3.3, and it is calculated for the previous study from the relationship  $F_{(H)} = \frac{S^2_{D(H)}}{S^2_{TE(H)}}$ . The values are given in Table 3.5

and demonstrate that, for each element, the total errors in the present study are significantly smaller than in the previous one.

#### 3.2.3.4. Partition of error variance.

Using the method described in Section 3.2.2, it is possible to partition the error variance into its component parts. Combined sub-sampling and analytical error variance,  $S^2_{ss+A(H)}$ , can be calculated from the 24 pairs of duplicate analyses given by Harrison and sampling error variance,  $S^2_{S(H)}$ , can be found from the data of Section 3.2.3.3, although

TABLE 3.5

Total error variance from previous and present studies.

Element	$S_{TE(H)}^2$	$S_{TE(R)}^2$	F	$F_c$
Cu	$1.19 \times 10^{-2}$	$1.77 \times 10^{-3}$	6.72	1.69
Pb	$2.10 \times 10^{-2}$	$1.60 \times 10^{-3}$	13.12	1.69
Zn	$2.86 \times 10^{-2}$	$3.19 \times 10^{-3}$	8.97	1.69
Fe	$1.84 \times 10^{-2}$	$3.64 \times 10^{-3}$	5.05	1.69
Mn	$2.73 \times 10^{-2}$	$1.50 \times 10^{-2}$	1.82	1.69

$F_c$  denotes critical F value at  $\alpha = 0.05$ .

the analytical error variance component cannot be isolated.

The comparison with the present study is tabulated in Table 3.6 which demonstrates that the techniques applied in the present study have led to a significant reduction in combined sub-sampling and analytical error variance for all elements at the 90% confidence level, and for all but Mn at the 95% level. In the previous study, 0.2g of minus 190 micron material was digested for one hour in 4M  $\text{HNO}_3$ , and analysed for Cu, Pb, Zn and Mn on a Perkin Elmer 290B (single-beam) Atomic Absorption Spectrophotometer. Fe was determined colorimetrically on the same acid leach. The improvement in combined sub-sampling and analytical error variance is attributed to the adoption of a technique using 0.5g of minus 125 micron material digested for 4 hours in 4M  $\text{HNO}_3$  and then analysed for all five elements on a Perkin Elmer 360 (twin-beam) instrument. Reasons for the significant reduction in sampling error variance are less easy to categorize, but it is possible that samples of larger bulk

TABLE 3.6

Comparison of sampling error variances and combined sub-sampling and analytical error variances for present and previous studies

Element	$S^2_{ss+A(H)}$	$S^2_{ss+A(R)}$	F	$F_c$	$S^2_{S(H)}$	$S^2_{S(R)}$	F	$F_c$
Cu	$1.57 \times 10^{-3}$	$5.46 \times 10^{-4}$	2.88	1.74	$1.03 \times 10^{-2}$	$1.22 \times 10^{-3}$	8.44	1.75
Pb	$1.22 \times 10^{-2}$	$2.32 \times 10^{-4}$	52.6	1.75	$8.80 \times 10^{-3}$	$1.37 \times 10^{-3}$	6.42	1.75
Zn	$1.60 \times 10^{-3}$	$5.74 \times 10^{-4}$	2.78	1.74	$2.70 \times 10^{-2}$	$2.62 \times 10^{-3}$	10.31	1.75
Fe	$9.04 \times 10^{-3}$	$1.05 \times 10^{-3}$	8.60	1.74	$9.36 \times 10^{-3}$	$2.58 \times 10^{-3}$	3.63	1.75
Mn	$1.56 \times 10^{-3}$	$9.37 \times 10^{-4}$	1.67	1.74* 1.54	$2.57 \times 10^{-2}$	$1.41 \times 10^{-2}$	1.82	1.75

$F_c$  denotes critical F value at  $\alpha = 0.05$

\* critical value of F at  $\alpha = 0.10$ .

were collected in the present study, filling sample bags of 27 cm x 12.5 cm dimensions. It is also possible that a more consistent separation was made between the sand-silt bed load, and an Fe rich precipitate covering parts of the stream bed (see Section 3.3.2).

### 3.3 EXAMINATION OF SAMPLING PROCEDURE

#### 3.3.1. Introduction

As Section 3.2.2.3. has highlighted the predominance of sampling error within total error variance, it is appropriate to consider some of the possible causes of sampling errors. The presence, in Yarner Stream, of large amounts of iron oxide-hydroxide precipitate is likely to affect attempts to collect consistently similar samples, and this possibility is investigated. Also the depth below the sediment/water interface at which samples were collected, which may influence Eh/pH conditions has been investigated. An attempt to determine how many "grabs" of sediment are necessary to obtain a sample representative of the stream at a locality was also made.

#### 3.3.2. Dependence of sampling error upon iron precipitation

When sampled, in March and April 1976, one of the most prominent features of Yarner Stream (see Fig. 1.2 ) was the presence from Pullabrook Farm (27930794) upstream to the mine at 27830784, of large amounts of bright orange, iron oxide-hydroxide jelly, in places up to 10 cm thick, covering much of the bed of the stream. At the time it was felt desirable that this apparently unrepresentative material should be excluded from samples of the sand-silt load of the stream, although quantities of it were collected separately, (see Plate 3).

Table 3.7 shows pairs of analyses of sand-silt sample and iron rich sample, each pair being from a different locality. Only Pb is consistently lower in the Fe rich samples, and the other elements show



PLATE 3

Yarner Stream at locality YW 23, showing prominent ferric  
hydroxide precipitate.

TABLE 3.7

Comparison of analyses of normal and Fe rich samples from various localities in Yarnier Stream.

The second of each pair is the Fe rich sample

Sample No.	Cu	Pb	Zn	Fe	Mn	As	Cd	Co	Ni
YW 5A	520	37	100	69000	680	2900	2	53	30
YW 5B	740	23	120	169000	410	9400	3	47	35
YW 11A	635	48	224	59000	740	3940	2	70	41
YW 11C	800	41	178	153000	1080	10900	2.5	98	38
YW 15A	560	39	216	52000	450	6300	2.5	30	37
YW 15C	3850	24	346	173000	2000	13100	5.5	183	67
YW 19A	450	52	292	47000	1400	2460	4	61	78
YW 19C	490	26	840	96000	17200	3740	11	220	171
YW 22A	585	64	310	64000	3900	3000	4.5	83	96
YW 22C	725	34	1130	163000	11000	8700	11.5	210	217

All values in ppm.

quite spectacular enrichment in some samples, and particularly those from close to the mine (higher sample numbers). It is to be expected that the presence of two types of material, with such obviously contrasting chemistry, will lead to serious sampling errors.

By dividing up the duplicate sample, and sub-sample pairs upon which the data in Section 3.2.2. is based, into those which occur in the Fe stained portion of the river, and those which do not, it is possible to demonstrate the effect which the Fe precipitate has on sampling and sub-sampling variance. Using Equations (3.7) and (3.4) it is possible to calculate the sampling variance in the Fe stained section,  $(S^2_{s(Fe)})$ , and in the non-Fe stained section,  $(S^2_{s(N)})$ , and also the combined sub-sampling and analytical variance in each section,  $S^2_{ss+A(Fe)}$  and  $S^2_{ss+A(N)}$ . The results, with the

appropriate F tests of significance at the 95% confidence level, are given in Tables 3.8 and 3.9.

TABLE 3.8

Comparison of sampling variance for Fe stained and non-Fe stained sections of Yarner Stream.

Element	$S^2_s(\text{Fe})$	$S^2_s(\text{N})$	F	$F_c$
Cu	$2.60 \times 10^{-3}$	$1.05 \times 10^{-4}$	24.76 (Fe>N)	2.03
Pb	$5.93 \times 10^{-4}$	$2.01 \times 10^{-3}$	3.39 (N>Fe)	2.04
Zn	$4.81 \times 10^{-3}$	$6.75 \times 10^{-4}$	7.13 (Fe>N)	2.03
Fe	$4.02 \times 10^{-3}$	$1.56 \times 10^{-3}$	2.58 (Fe>N)	2.03
Mn	$2.07 \times 10^{-2}$	$9.06 \times 10^{-3}$	2.28 (Fe>N)	2.03
As	$4.77 \times 10^{-3}$	$1.81 \times 10^{-3}$	2.64 (Fe>N)	2.04
Co	$5.83 \times 10^{-3}$	$1.90 \times 10^{-3}$	3.07 (Fe>N)	2.04
Ni	$2.92 \times 10^{-3}$	$2.44 \times 10^{-3}$	1.20	2.04

Results for Cd are not quoted because of detection limit problem outlined in Section 3.2.2.3.

$F_c$  denotes critical value of F at  $\alpha = 0.05$ .

TABLE 3.9

Comparison of combined sub-sampling and analytical variances for Fe stained and non-Fe stained sections of Yarner Stream.

Element	$S^2_{ss+A}(\text{Fe})$	$S^2_{ss+A}(\text{N})$	F	$F_c$
Cu	$5.66 \times 10^{-4}$	$5.73 \times 10^{-4}$	1.01	1.98
Pb	$1.85 \times 10^{-4}$	$3.83 \times 10^{-4}$	2.07	2.09
Zn	$4.86 \times 10^{-4}$	$7.93 \times 10^{-4}$	1.63	1.98
Fe	$1.16 \times 10^{-3}$	$8.84 \times 10^{-4}$	1.32	1.98
Mn	$9.89 \times 10^{-4}$	$8.89 \times 10^{-4}$	1.11	1.98
As	$2.48 \times 10^{-4}$	$6.15 \times 10^{-4}$	2.48	2.51
Co	$5.77 \times 10^{-4}$	$7.90 \times 10^{-4}$	1.37	2.45
Ni	$7.80 \times 10^{-4}$	$4.64 \times 10^{-4}$	1.68	2.51

Results for Cd are not quoted because of detection limit problem outlined in Section 3.2.2.3.  $F_c$  denotes critical value of F at  $\alpha = 0.05$ .

Table 3.8 demonstrates that, except for Pb and Ni, sampling variance is greater where iron precipitation occurs, than where it does not. In the case of Pb, the variance is greater in the non-Fe stained sections of the stream, probably reflecting that the level of Pb present in the Fe jelly is lower than in the sand-silt bed load. In the case of Ni, although the variance in the Fe stained section is greater than that outside it, the difference is not significant, even at the 99% confidence level.

Table 3.9 shows that, at the 95% confidence level, the position in the stream makes no significant difference to the sub-sampling and analytical variance, which is much as might, intuitively, be expected.

Thus, the mixing of metal rich, iron oxide-hydroxide precipitate with the sand-silt bed load of the stream has been shown to be a significant source of sampling variance, but not a source of sub-sampling and analytical variance.

### 3.3.3. Dependence of sampling error upon depth of sampling, and number of "grabs" of sediment taken

Five pairs of samples were collected on the surface of, and at 5 cm depth into, a conveniently large bank of sediment at 27770783, in a right bank tributary of Yarner Stream, in order to evaluate what effects, if any, depth below the sediment/water interface has on metal content. In evaluating the results, each surface sample was set to a value of 100% and the 5 cm depth sample was calculated as a percentage of the surface one. The results are given in Table 3.10.



TABLE 3.10

The effect of depth of sampling on metal content of a sediment. Values given are those of the at-depth sample expressed as a percentage of the surface one.

Pair Number	Cu	Pb	Zn	Fe	Mn	As	Cd	Co	Ni
1	126%	98%	97%	116%	95%	126%	121%	106%	108%
2	127%	120%	161%	143%	250%	205%	200%	186%	182%
3	152%	159%	246%	225%	427%	457%	378%	268%	199%
4	146%	126%	324%	205%	557%	360%	282%	285%	292%
5	140%	119%	249%	252%	405%	437%	287%	222%	231%
Mean	138%	124%	215%	188%	347%	317%	254%	213%	202%

As can be seen from the results, the overall effect is that samples collected at 5 cm depth are substantially higher in metal than those from the surface of the sediment bank at this locality. This increase is most marked for Mn, which, for the 5 pairs of samples, averages 347% higher than the surface samples. These findings are in contrast to those of Plant (1971) who argues that, because Mn and Fe are soluble in the lower Eh conditions below the sediment/water interface, the concentration of metals in sediment from below the interface will be lower than on the surface where Fe and Mn are insoluble and precipitated.

As the present study was confined to only one locality, it would be presumptuous to draw any firm conclusions from this observation, save that the depth of sampling may have a very considerable effect on sampling error and deserves more detailed study. Further, until more is known about the distribution of metals and of Eh/pH conditions with respect to depth of burial, perhaps sampling should be confined to material available at the sediment/water interface. Indeed, since many streams, particularly those in headwaters, entirely lack sediment banks, it is only possible to sample sediment from that interface.

Samples were collected at the same locality compounded from 1, 2, 3 and 5 handfuls of sediment, ten composites of each size being collected. The results are summarized in Table 3.11. Significant reductions in variance are achieved for Pb, Zn, Fe and Mn when the number of grabs increases from 1 to 3. This trend is not so apparent when comparing the results of 1 grab versus 5. This may be due to the fact that by the time the fourth and fifth grabs of sediment were being collected a substantial hole had been dug into the sediment bank and the material from deeper in the bank was probably different in metal content to that at the top, as was shown earlier in this section.

TABLE 3.11

The effect of number of handfuls of sediment upon the variance of the samples produced.

Element	$S_1^2$	$S_2^2$	$S_3^2$	$S_5^2$	$F_{1-3}$	$F_{1-5}$
Cu	$1.04 \times 10^{-3}$	$7.64 \times 10^{-4}$	$6.58 \times 10^{-4}$	$6.34 \times 10^{-4}$	1.58	1.64
Pb	$1.30 \times 10^{-3}$	$4.04 \times 10^{-4}$	$3.59 \times 10^{-4}$	$8.98 \times 10^{-4}$	3.62**	1.45
Zn	$1.43 \times 10^{-2}$	$9.19 \times 10^{-3}$	$2.37 \times 10^{-3}$	$3.45 \times 10^{-3}$	6.03**	4.14**
Fe	$8.20 \times 10^{-3}$	$3.98 \times 10^{-3}$	$2.48 \times 10^{-3}$	$3.35 \times 10^{-3}$	3.31**	2.45*
Mn	$4.16 \times 10^{-2}$	$2.51 \times 10^{-2}$	$4.35 \times 10^{-3}$	$1.02 \times 10^{-2}$	9.56**	4.08**

Where  $S_i^2$  is the variance of the logarithms of the ten samples made up of  $i$  grabs of sediment.

$F_{1-3}$  is the F ratio between  $S_1^2$  and  $S_3^2$ .

$F_{1-5}$  is the F ratio between  $S_1^2$  and  $S_5^2$ .

Critical F value at  $\alpha = 0.05$  is 3.18 and at  $\alpha = 0.10$  is 2.44.

\*\* indicates difference significant at 95%.

\* indicates difference significant at 90%.

### 3.4 EXAMINATION OF VARIABLE SAMPLING PRECISION

Miesch (1967) defines the significance of a particular geochemical attribute in terms of the following equation:-

$$X_{ij} = \mu + \beta_i + \omega_{ij} ,$$

where  $X_{ij}$  is the attribute of the jth specimen from the ith locality.

$\mu$  is the grand mean of the "rock body"

$\beta_i$  is deviation of the ith locality mean from grand mean,  $\mu$

$\omega_{ij}$  is deviation of the jth sample from ith locality mean.

Thus  $\omega_{ij}$  (the sampling error) is the difference between the concentration of an element in an individual specimen ( $X_{ij}$ ) and the true mean concentration for that locality ( $\mu + \beta_i$ ). It is impossible to obtain the true value for a locality, as this requires that all possible samples from a locality be collected and analysed by a perfectly accurate and precise method.

Miesch (op. cit.) defines four critical aspects of error as overall bias, variable bias, variable precision and normality of error distribution. Overall and variable bias may only be assessed if the true locality mean value is known, and considerable departures from normality can often be tolerated, and corrected for by suitable transformations. However, variable sampling precision can be assessed since, in its absence, the variation of sampling error should tend to be the same for each locality as the number of specimens per locality increases, i.e.

$$\frac{1}{n_1-1} \sum_{j=1}^{n_1} (\omega_{1j} - \bar{\omega}_1)^2 \rightarrow \frac{1}{n_2-1} \sum_{j=1}^{n_2} (\omega_{2j} - \bar{\omega}_2)^2 \dots \rightarrow \frac{1}{n_i-1} \sum_{j=1}^{n_i} (\omega_{ij} - \bar{\omega}_i)^2$$

as  $n_1, n_2, \dots, n_i \rightarrow \infty$  where  $\bar{\omega}_i$  is the mean sampling error at locality i.

If the variance of  $\omega_{ij}$  at locality  $i$  is denoted as  $S_{\omega i}^2$ , the above equation may be re-written as:-

$$S_{\omega 1}^2 \rightarrow S_{\omega 2}^2 \dots \rightarrow S_{\omega i}^2 \quad \text{as} \quad n_1, n_2, \dots n_i \rightarrow \infty. \quad (3.10)$$

If this condition does not hold, variable sampling precision is present. If analytical errors are small, the above may be tested by assuming that

$$\omega_{ij} - \bar{\omega}_i = X_{ij} - \bar{x}_i,$$

where  $\bar{x}_i$  is the mean value for all samples collected at locality  $i$ , and the other symbols are as previously defined. Therefore Equation (3.10) may be re-written as:-

$$S_{x1}^2 \rightarrow S_{x2}^2 \dots \rightarrow S_{xi}^2 \quad \text{as} \quad n_1, n_2, \dots n_i \rightarrow \infty.$$

Twenty samples were collected at each of ten localities in the River Mardle, (see Fig.1.3 ) between Brookmill (27240675) and Bilberryhill Farm (27270668). Half a gramme of minus 125 micron material from each sample was analysed by AAS for Cu, Pb, Zn, Fe and Mn, following a four hour digestion in 4M  $\text{HNO}_3$ . Thus, a locality mean for each element can be calculated, and having arranged the 20 analyses in random order, 19 values of

$$\frac{1}{n_i - 1} \sum_{j=1}^{n_i} (X_{ij} - \bar{x}_i)^2$$

can be calculated as  $n_i$  is increased from 2 to 20.

The results of these calculations are summarised in Table 3.12. For each value of  $n$  given in the Table, the standard deviation of the 10 variances is quoted. For Cu, Pb, Zn and Mn the lowest standard deviation is for the  $n = 20$  situation and for Fe its increase over the  $n=15$  value is only slight. This means that the variances for the various sites are approaching each other as  $n$  increases and that the conditions of Equation (3.10) are being fulfilled, indicating that variable sampling precision is absent.

TABLE 3.12

Summary of variances for each element at each site and certain values of n.

Cu

Site	n=5	n=10	n=15	n=20
RM 1	1102	1590	2040	3145
RM 2	13812	11908	9972	8810
RM 3	628	737	921	1150
RM 4	9362	4508	3445	3680
RM 5	1279	4254	3398	2619
RM 6	1330	4212	5476	4637
RM 7	2399	1765	6454	5757
RM 8	3325	2803	3298	3422
RM 9	4454	3557	3169	2732
RM10	36182	18485	14494	12638
SD	10972	5545	4125	3443

SD denotes Standard Deviation of variances for sites RM 1 to RM10, for given values of n.

Pb

Site	n=5	n=10	n=15	n=20
1	431	328	618	595
2	372	402	343	281
3	54	51	60	47
4	305	181	247	222
5	13	78	87	68
6	54	111	120	108
7	687	455	360	345
8	72	60	100	132
9	127	122	105	106
10	5138	2335	1599	1224
SD	1565	691	468	360

Zn

Site	n=5	n=10	n=15	n=20
1	7184	3693	2763	2169
2	150	662	529	515
3	255	221	190	183
4	285	258	3370	2689
5	169	376	260	264
6	119	86	188	197
7	819	454	323	339
8	217	221	173	240
9	531	312	260	249
10	375	623	583	634
SD	2180	1070	1178	906

TABLE 3.12 ... continued ...

Summary of variances for each element at each site and certain values of n

<u>Fe</u>	all x 10 <sup>6</sup>			
Site	n=5	n=10	n=15	n=20
1	2.27	2.05	2.24	3.58
2	3.64	2.74	3.57	2.99
3	0.59	1.92	2.29	2.44
4	5.27	3.35	4.37	3.94
5	2.17	3.34	3.14	2.64
6	0.89	1.29	1.39	1.20
7	2.88	1.68	2.42	2.94
8	5.65	3.34	3.11	3.85
9	5.83	4.79	3.53	3.62
10	7.47	8.47	7.27	7.87
SD	2.30x10 <sup>6</sup>	2.09x10 <sup>6</sup>	1.62x10 <sup>6</sup>	1.71x10 <sup>6</sup>

<u>Mn</u>				
Site	n=5	n=10	n=15	n=20
1	2135	1278	1863	2426
2	15030	11985	8590	8140
3	562	1665	1995	2017
4	10781	6170	7872	6652
5	6256	5946	4350	3418
6	4778	4841	4603	3608
7	3050	3256	4711	4145
8	5121	4588	3624	4200
9	3872	5214	4754	4372
10	19133	12610	10180	9609
SD	6013	3822	2765	2408

### 3.5 CONCLUSIONS

A detailed field investigation, using duplicate sampling, sub-sampling and analysis, has been carried out at Yarner Wood, south Devon. The results have shown that, firstly, the total data variance is very significantly greater than the total error variance. Also the fact that variance is an additive quantity has been used to sub-divide error variance between sampling error, sub-sampling error and analytical error. For the eight elements to which this technique could be applied, analytical errors ranged from 0.7% to 16.9% of total error, sub-sampling error from 1.1% to 25.8% and sampling error from 57.3% to 93.8% of total error. It is thus demonstrated that sampling is the dominant source of error, and that better understanding of this procedure will be the key to better overall data reproducibility. For Cd the total error variance value was actually marginally smaller than the combined analytical and sub-sampling variance value. This reflects the fact that the levels of Cd in these samples are very close to the detection limit of the instrument and therefore further interpretation of Cd results can, at best, be only qualitative.

Comparison has been made between the present study and that of Harrison (1974). This shows that, whilst overall data variance is comparable for both studies, significant reductions in total error variance, sampling error variance and combined analytical and sub-sampling error variance have been achieved by the optimised techniques devised during the present study.

An examination of sampling error, the main component of total error, has shown that the ferric oxide-hydroxide precipitate present in large quantities in parts of Yarner Stream contributes significantly to sampling error, but it makes no appreciable difference to combined sub-sampling and analytical errors.



Changes in Eh and pH below the sediment-water interface, causing alterations in Mn and Fe solubility, may be responsible for the significant differences in metal content between surface samples and samples gathered at depth below the interface. It is not felt that the present very limited study of this phenomenon is in any way adequate. Its findings are partially in conflict with those of Plant (1971), and serve to highlight the need for more detailed work. In the meantime, it may be advisable to restrict sample collection to material available at the water/sediment interface.

The findings of an experiment, aimed at determining how many handfuls of sediment constitute a representative sample at a given locality, have been largely rendered invalid by the metal variation with depth described above.

Variances around the site mean of 20 samples collected at each of 10 sites in the River Mardle have been calculated in order to determine whether or not variable sampling precision, as defined by Miesch (1967), is present. It may be concluded from the results for Cu, Pb, Zn, Fe and Mn that variable sampling precision is largely absent.

## CHAPTER 4

### VARIABILITY INTRODUCED DURING SAMPLE PREPARATION

#### 4.1 INTRODUCTION

#### 4.2 DRYING OF SAMPLES

4.2.1. Delays before drying

4.2.2. Temperature of drying

#### 4.3 SIEVING AND SPLITTING

4.3.1. The Mechanics of Sieving

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4.3.3.1. Introduction

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#### 4.4 SUB-SAMPLING

#### 4.5 CONCLUSIONS

## CHAPTER 4

### VARIABILITY INTRODUCED DURING SAMPLE PREPARATION

#### 4.1 INTRODUCTION

Prior to analysis, applied geochemical samples are subjected to a number of processes, here collectively referred to as Sample Preparation. These processes are seldom referred to in the literature, and it therefore seems likely that standard practice at present is based on "rule of thumb" and tradition rather than experiment.

The manner in which stream sediment samples are dried was one subject of investigation. Samples were kept wet for up to 53 days before drying and analysis. In addition, an attempt was made to investigate whether the chemical composition of samples is affected by drying at temperatures of up to 500°C.

A Griffin and George Vibratory Ball Mill, adapted for shaking, was used throughout for sieving, in order to achieve a uniform action. The proportions of bulk sample material passing each of the 6 mesh sizes used was recorded. Samples were divided, where necessary, using a Pascall Engineering rotating sample splitter, and data concerning bias introduced by this apparatus is presented.

A further experiment investigated the composition of material passing through a sieve at various intervals of shaking time. It was anticipated that the base-metal rich fine particles would pass through the sieve very quickly, and that as sieving time increases, so coarser metal-poor material will be forced through. Some of the samples upon which investigation was attempted showed this not to be the case, and highlight the need for caution and standardisation in sieving technique.

An attempt was made to examine the possible effects of sub-sampling, and of settling within a packet of sieved material. It is by no means uncommon for samples to be air-freighted from collection area to

laboratory, and in-flight vibration is a possible cause of un-mixing.

## 4.2 DRYING OF SAMPLES

### 4.2.1. Delays before drying

Berina and Genberga (1971) have reported that levels of Cu and Fe in soil samples vary during the drying process and in order to extend this idea to stream sediments thirty samples were collected from large sediment banks at each of two localities in Yarner Wood (27780773 and 27770774) (see Fig. 1.2 ). A control set of 10 samples from each locality was dried, the same day as collected, in a hot air oven at 80°C. The remaining 20 samples from each locality were divided into two groups. Group A samples were stored in the open air until required for drying, and Group B samples were stored in a sealed plastic bag until removed for drying. Corresponding samples from both groups and both sites were dried at 80°C after the following time intervals, all in days, 1, 2, 4, 6, 9, 14, 19, 29, 39, 52. Analysis of 0.5g of minus 125 micron material was carried out by AAS for Cu, Pb, Zn, Fe and Mn, after 4 hours digestion in 4M HNO<sub>3</sub>.

The results for the control sets are shown in Tables 4.1 and 4.2. The means and standard deviations were calculated via a log<sub>10</sub> transformation and the confidence intervals of mean  $\pm$  2 standard deviations are the antilogs of the log<sub>10</sub> transformed statistics. Tables 4.3 and 4.4 show the results for the A and B sets of samples which were dried at various times after collection. Those samples which fall outside the confidence limits quoted for the control set are indicated.

The results for sample 19A (Table 4.3) are consistently higher than the control set limits and in view of the dissimilarity of this sample to the others from this locality, it seems sensible to exclude it from further consideration. The remaining samples from this locality show

TABLE 4.1

Control set of 10 samples from drying locality 1

Sample No.	Cu	Pb	Zn	Fe	Mn
1	73	33	33	13500	356
2	81	36	34	11500	280
3	60	29	30	12000	296
4	62	30	30	12500	264
5	56	27	25	9500	196
6	49	25	24	7050	156
7	71	32	30	11000	208
8	70	32	29	9550	212
9	71	32	30	9200	232
10	82	38	33	12000	232
Mean *	1.8242	1.4938	1.4718	4.0257	2.3752
Standard Deviation*	0.0711	0.0544	0.0494	0.0836	0.1019
Mean + 2 SD**93		40	37	15595	379
Mean - 2 SD**48		24	24	7219	148

\* Data  $\log_{10}$  transformed.\*\* Antilog of  $\log_{10}$  transformed statistics.

All values in ppm.

TABLE 4.2

Control set of 10 samples from drying locality 2.

Sample No.	Cu	Pb	Zn	Fe	Mn
1	125	74	335	35000	3800
2	122	70	345	33000	4400
3	133	66	330	39000	4400
4	114	77	320	36500	3800
5	121	74	370	39000	5600
6	141	78	830	66500	20900
7	147	86	630	68500	13700
8	146	90	530	54000	9900
9	141	86	470	51000	8000
10	134	77	755	63500	17400
Mean *	2.1204	1.8891	2.6674	4.6708	3.8791
Standard Deviation*	0.0380	0.0421	0.1576	0.1232	0.2815
Mean + 2 SD**	157	94	955	82642	27670
Mean - 2 SD**	111	64	224	26570	2071

\* Data  $\log_{10}$  transformed.\*\* Antilog of  $\log_{10}$  transformed statistics.

All values in ppm.

no variation beyond the control set limits for Cu, Pb and Zn but show erratic changes in level, mostly downwards, for Fe and Mn from samples 11 to 20. Of the samples from locality 2, (Table 4.4), only four show variation beyond the limits of the control samples, all of these are upward, three of them are for Zn, the remaining one being for Fe.

Significant variations in the metal content of samples which have been stored prior to drying have been confirmed, even in samples stored for no longer than 1 day, highlighting the importance of completely drying samples as soon as possible after collection. No reason for this variation is immediately apparent. It may, however, be that water held between the grains of the wet samples, in conditions of falling Eh, dissolves Fe and Mn, and also Zn which is closely associated with Mn (see Section 8.2.5, Chapter 8). When the sample is then dried some of the dissolved material may be removed altogether, and the degree to which such dissolved material goes back into the sample and the chemical form it takes if re-precipitated, may result in the observed variations. Thus, in order to minimise any such variations, samples ought to be dried thoroughly at the earliest possible opportunity.

#### 4.2.2. Temperature of drying

Since it seems desirable that samples should be completely dried as soon as possible after collection, it is logical to investigate speeding the process by using a higher drying temperature than the 80°C-95°C commonly employed. Minus 140 micron material from bulk sample sites B and G was dried at 80°C and then, in batches of 5 x 1.0g, subjected to 2 hours further drying at the following temperatures, 150°C, 200°C, 300°C and 500°C. Analysis of 0.5g sub-samples by AAS for Cu, Pb, Zn, Fe, Mn, As and Co followed a 4 hour digestion in 4M HNO<sub>3</sub> at 95°C.

TABLE 4.3

A and B sets from drying locality 1.

Sample No.	Cu		Pb		Zn		Fe		Mn	
	A	B	A	B	A	B	A	B	A	B
11	60	55	28	26	25	25	7900	5700*	124*	88*
12	70	76	31	32	33	29	8900	8750	284	124*
13	83	88	39	37	36	35	13500	12500	440**	212
14	86	77	36	33	30	33	10500	6900*	156	84*
15	67	63	29	32	25	35	6600*	7350	92*	152
16	67	71	28	29	25	31	5250*	5100*	80*	100*
17	58	81	27	36	24	35	4850*	13500	116*	252
18	82	78	37	37	28	36	14000	18500**	280	372
19	103**	83	52**	38	38**	37	26000**	14000	428**	292
20	85	90	39	35	27	35	14000	8300	260	136*

\*\* Indicates greater than Mean + 2 SD of control set.

\* Indicates less than Mean - 2 SD of control set.



## A and B sets from drying locality 2.

Sample No.	Cu		Pb		Zn		Fe		Mn	
	A	B	A	B	A	B	A	B	A	B
31	153	141	89	84	680	565	77500	58000	16200	11600
32	130	133	76	80	525	935	57500	72000	10800	17100
33	133	127	85	74	640	555	63500	55000	13900	11200
34	114	133	77	84	350	695	49000	76000	6800	16800
35	120	123	79	77	460	535	51000	52000	8300	10000
36	120	140	77	88	555	745	54500	70000	11500	17000
37	142	113	78	72	955**	450	69500	49000	21900	8800
38	134	128	88	85	595	595	58500	61500	12200	13100
39	146	146	88	91	955**	870	83000**	78000	24300	19400
40	123	146	72	84	930	975**	62500	77000	20900	23300

\*\* Indicates greater than Mean + 2 SD of control set.

\* Indicates less than Mean - 2 SD of control set.

Means and standard deviations were calculated for each group of five analyses. Comparisons between samples treated at 80°C and 150°C and at 80°C and 500°C were effected using F tests to compare variances, and where the variances proved similar, t tests to compare means (see Till, 1974, p.61). Where the variances were dissimilar at the 95% level, comparison of means was effected by recourse to Standard Error of the Difference (Moroney, 1953, p.220). The results are summarised in Tables 4.5, 4.6 and 4.7.

At the low temperature of 150°C significant differences are shown by only 2 elements Pb and Fe, in material from site B, and none from Site G. However, at the maximum temperature tested, 500°C, significant differences are shown by all elements except Mn at Site B, and by Pb, As and Co at Site G. Differences in the elemental composition of samples treated at high temperatures may well relate to changes, with rising temperature, in clay mineralogy. This is supported by the fact that Site B material, which shows the more pronounced effects, is more clay-rich than Site G material since only 19% of minus 70 micron material from Site G is light mineral (concentration done on Micropanner) whilst for Site B this figure is 86.6%.

The fact that changes do occur must preclude the use of elevated drying temperatures during sample preparation, although further work within the range 70°C to 150°C might be useful to see how critical the chosen temperature is. A further consideration which should be made when drying samples is the ignition point of the paper commonly used for making sample bags. Obviously it is cumbersome to have to remove samples from their paper bags for drying, and highly inconvenient if the bags should burn during drying. Sample bags, in fact, become brittle at about 150°C and burn at about 300°C, therefore temperatures in excess of 150°C are inadvisable unless samples are removed from their paper bags.

TABLE 4.5 Mean and Standard Deviation statistics for each treatment temperature.

Treat- ment Temp.	Cu B		Pb B		Zn B		Fe B		Mn B		As B		Co B	
	Mean	S.D.	Mean	S.D.	Mean	S.D.	Mean	S.D.	Mean	S.D.	Mean	S.D.	Mean	S.D.
80°C	98.0	7.87	68.8	1.92	157.4	11.50	24040	1410	916	75.0	406	49.3	27.6	2.07
150°C	97.4	3.51	62.2	2.95	152.2	10.11	22400	547.7	882	48.7	404	65.0	25.8	1.48
200°C	96.8	5.50	62.3	2.86	154.0	8.88	22960	1438	878	51.2	430	49.5	27.4	2.30
300°C	95.2	1.79	66.2	1.79	157.6	5.68	24400	1241	900	37.4	428	52.6	26.8	1.30
500°C	106.8	1.92	75.4	4.83	171.8	6.91	26560	296.6	952	65.0	492	45.5	31.2	1.64

	Cu G		Pb G		Zn G		Fe G		Mn G		As G		Co G	
	Mean	S.D.	Mean	S.D.	Mean	S.D.	Mean	S.D.	Mean	S.D.	Mean	S.D.	Mean	S.D.
80°C	544	20.1	5740	356	503	53.9	39800	2387	1144	72.7	286	16.7	64.6	2.88
150°C	545	23.4	5820	231	477	20.2	39600	1673	1104	18.2	302	23.9	64.8	3.11
200°C	548	12.0	5790	185	500	21.5	39200	1095	1102	29.5	280	25.5	62.2	1.10
300°C	546	18.8	5740	129	494	20.7	40000	3391	1102	27.5	284	23.0	62.2	2.77
500°C	540	24.7	6130	329	510	40.6	39000	1225	1118	48.7	248	19.2	59.4	2.61

All values in ppm. In each case n = 5.

TABLE 4.6 Comparison of results for sample treated at 80°C and 150°C

Site B

Cu	F = 5.02*	Sp = 6.81	t = 0.14	NS
Pb	F = 2.36	Sp = 2.78	t = 3.75	SIG***
Zn	F = 1.29	Sp = 12.11	t = 0.42	NS
Fe	F = 6.63**	SED = 676	Diff. = 1640 = 2.4xSED	SIG**
Mn	F = 2.38	Sp = 70.7	t = 0.76	NS
As	F = 1.74	Sp = 64.5	t = 0.05	NS
Co	F = 1.96	Sp = 2.01	t = 1.42	NS

Site G

Cu	F = 1.36	Sp = 24.4	t = 0.06	NS
Pb	F = 2.38	Sp = 335	t = 0.38	NS
Zn	F = 7.13**	SED = 25.75	Diff. = 26 = 1.01xSED	NS
Fe	F = 2.04	Sp = 2305	t = 0.14	NS
Mn	F = 15.99**	SED = 33.5	Diff. = 40 = 1.19xSED	NS
As	F = 2.04	Sp = 23.0	t = 1.10	NS
Co	F = 1.17	Sp = 3.35	t = 0.09	NS

In all cases  $n = 5$

Sp denotes Pooled Estimate of Standard Deviation.

t denotes Student's t statistic.

SED denotes Standard Error of Difference.

Diff. denotes Difference in means,  $\bar{x}_1 - \bar{x}_2$ .

NS denotes no significant difference in means.

SIG denotes difference in means is significant.

\* denotes significant at  $\alpha = 0.10$ .

\*\* denotes significant at  $\alpha = 0.05$ .

\*\*\* denotes significant at  $\alpha = 0.01$ .

TABLE 4.7 Comparison of results for samples treated at 80°C and 500°C

Site B

Cu	F = 16.89***	SED = 3.62	Diff. = 8.8=2.43xSED	SIG**
Pb	F = 6.33*	Sp = 4.11	t = 2.54	SIG**
Zn	F = 2.77	Sp =10.61	t = 2.15	SIG*
Fe	F = 22.6***	SED = 644	Diff. = 2520=3.91xSED	SIG***
Mn	F = 1.33	Sp =78.5	t = 0.73	NS
As	F = 1.17	Sp =53.0	t = 2.56	SIG**
Co	F = 1.59	Sp = 1.92	t = 2.96	SIG**

Site G

Cu	F = 1.51	Sp =25.2	t = 0.25	NS
Pb	F = 1.17	Sp=382.2	t = 1.88	SIG*
Zn	F = 1.76	Sp =53.4	t = 0.21	NS
Fe	F = 3.80	Sp = 2121	t = 0.60	NS
Mn	F = 2.23	Sp =69.1	t = 0.60	NS
As	F = 1.32	Sp =20.2	t = 2.98	SIG**
Co	F = 1.22	Sp = 3.07	t = 2.68	SIG**

For legend see Table 4.6

### 4.3 SIEVING AND SPLITTING

#### 4.3.1. The Mechanics of Sieving

All sieving, except for the experiment described in Section 4.3.3, was conducted mechanically on a Griffin and George Vibratory Ball Mill, adapted for shaking, thus achieving a systematic sieving motion (see Plate 4 ). Samples of similar origin were sieved for identical time periods so that the degree to which particles, close to the mesh size, are forced through is similar.

The establishment of a time period for sieving material from the five bulk sediment samples was done with reference to material from Site B. During a pilot run, sieving 2 kg of minus 2 mm sample to determine the approximate proportions of the various mesh fractions, the amount of material passing certain mesh sizes in various periods of time was noted. In two separate instances, using a 660 micron sieve, increasing the sieving time from 30 to 60 secs. caused an extra 8% and 12.5% of material to pass the screen. Increasing the time, in the second instance, by further 30 second periods, up to 120 secs. in all, caused increases of 2.5% and 2.0% respectively. Thus, increasing the sieving time from 30 to 120 secs., caused an overall increase of 17.6% in the amount of material passing the screen. An extra 60 secs., making 3 mins. in all, when sieving at 190 microns, produced an extra 5% of minus 190 micron material. However, visual examination of this material showed it to be sand-sized, and close to the maximum size the screen passes. The extra 60 secs. was not considered worthwhile, and a sieving time of 2 minutes was set as standard.

Table 4.8 shows how much material would have passed, and how much would have been retained, by each of the meshes used, had portions of individual fractions not been set aside for various experiments. The particle size composition of the samples is illustrated in Figure 4.1.

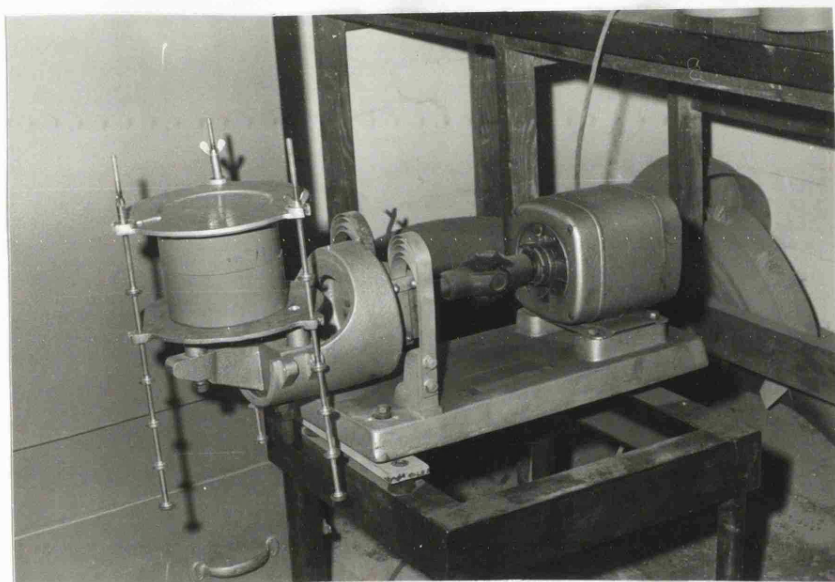


PLATE 4

Griffin and George vibratory ball mill, adapted for shaking.

TABLE 4.8 Theoretical proportions of various size fractions from bulk sample sites B, G, O, P and Y.

Site B Total sample weight 31,225

Mesh size (microns)	weight passed	weight retained	Retained size (microns)	% of total passed screen
2000	21080	10145	+2000	67.5
660	8778	12302	-2000+660	28.1
190	2203	6575	- 660+190	7.1
140	1500	703	- 190+140	4.8
125	1092	408	- 140+125	3.5
70	533	559	- 125+ 70	1.7

Site G Total sample weight 38,820

2000	35190	3630	+2000	90.6
660	22728	12462	-2000+660	58.5
190	4489	18239	- 660+190	11.6
140	2590	1899	- 190+140	6.7
125	1637	953	- 140+125	4.2
70	545	1092	- 125+ 70	1.4

Site O Total Sample weight 50,420

2000	39105	11315	+2000	77.6
660	6939	32166	-2000+660	13.8
190	439	6500	- 660+190	0.9
140	272	167	- 190+140	0.5
125	168	104	- 140+125	0.3
70	42	126	- 125+ 70	0.1

Site P Total sample weight 49,580

2000	28165	21415	+2000	56.8
660	13987	14178	-2000+660	28.2
190	2747	11240	- 660+190	5.5
140	1778	969	- 190+140	3.6
125	1237	541	- 140+125	2.5
70	546	691	- 125+ 70	1.1

Site Y Total Sample weight 40310

2000	35605	4705	+2000	88.3
660	17319	18286	-2000+660	43.0
190	2089	15230	- 660+190	5.2
140	1359	730	- 190+140	3.4
125	948	411	- 140+125	2.4
70	469	479	- 125+ 70	1.2

All sample weights in grammes.



This shows that for all five samples, the vast majority of the minus 2 mm material is coarser than 190 microns. All five samples also show a minimum in the minus 140 plus 125 micron fraction, which implies that a degree of bimodality is present in the size distribution of particles even though the individual streams have their headwaters in different geological environments. This bimodality may reflect the fact that material coarser than 140 microns is still large enough to be physically abraded in a stream, where particles finer than 125 microns will tend to be cushioned from abrasion and therefore persist in the bed load.

#### 4.3.2. Splitting

When dividing bulk samples into component parts, it is frequently necessary to take a small portion, perhaps only a few tens or hundreds of grammes, to be representative of a much larger weight of material. The standard method of "Coning and Quartering" can be simulated mechanically by using a rotating sample splitter, such as that made by Pascall Engineering (see Plate 5 ). The material to be divided is placed in a hopper, and allowed to fall onto a cone which passes the material into the six rotating containers beneath.

The six containers were assembled each time in the same order, and placed in the same position on the rotating base. Thirty-five runs with this machine, using material from all five bulk sample sites were weighed after completion of the process. Each of the six weighings was standardised using the mean and standard deviation of the set of six. Then the mean and variance of the 35 standardised values for each container were calculated and are shown in Table 4.9

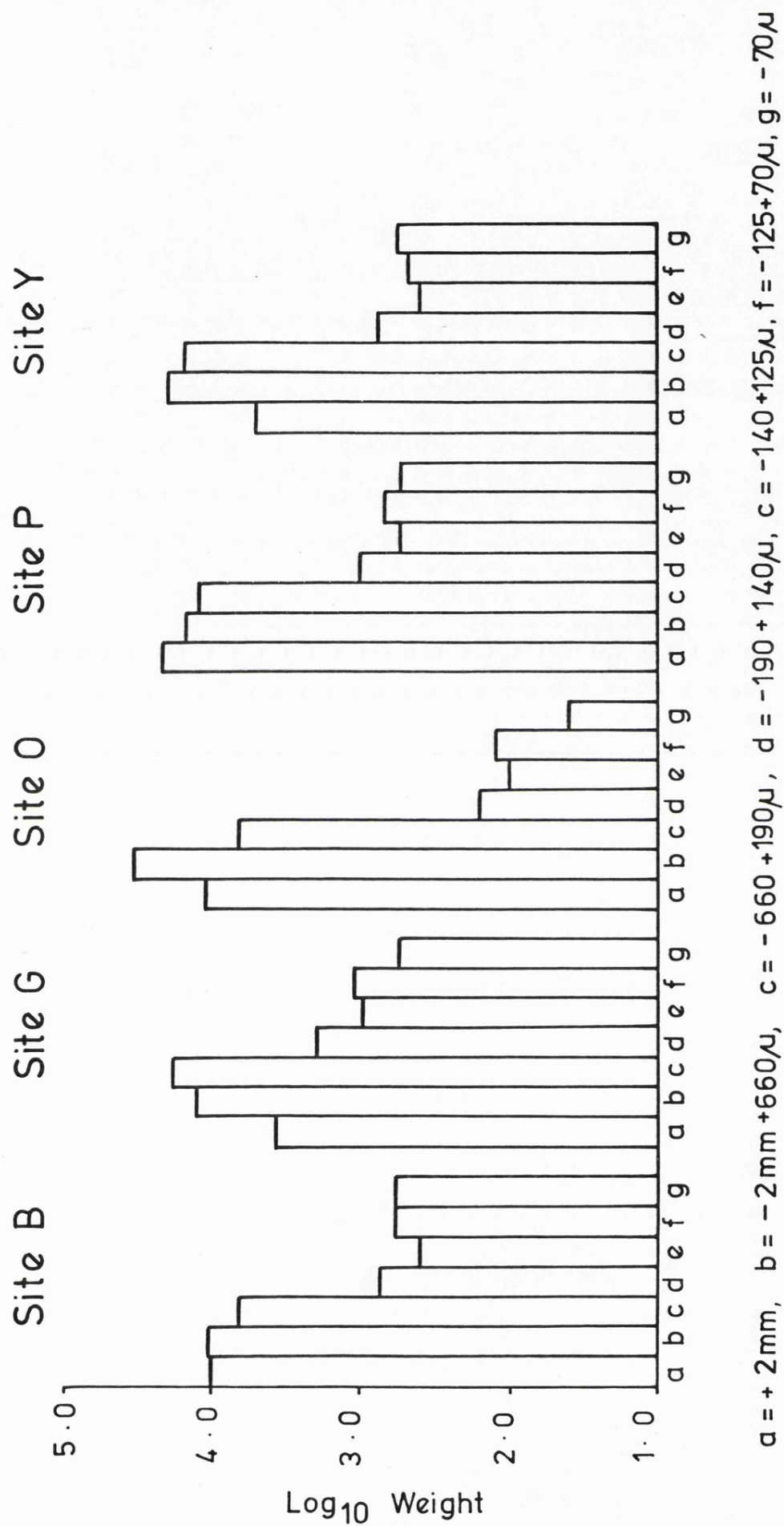


FIG. 4.1 DISTRIBUTION OF PARTICLE SIZES, ALL BULK SAMPLES

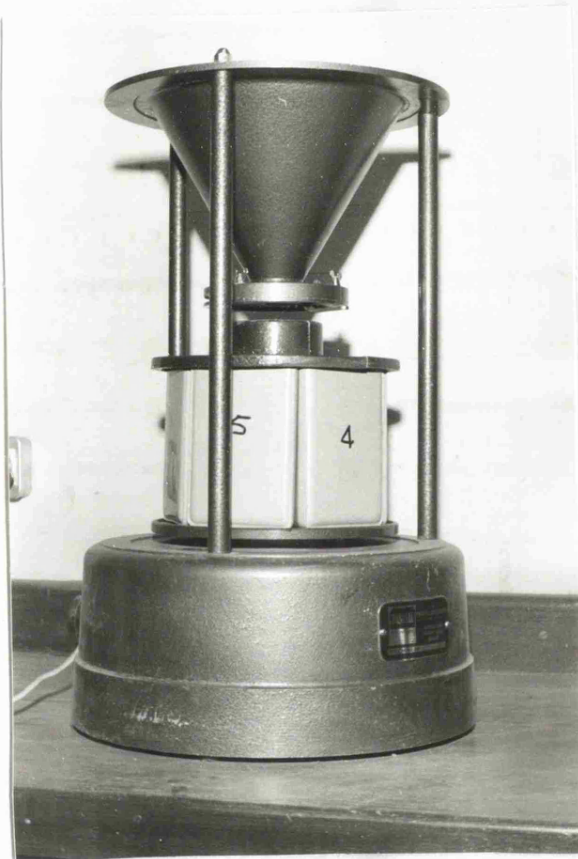


PLATE 5

Pascall Engineering sample splitter.

TABLE 4.9 Mean and variance of standardised data for each of the six containers in the Pascall Splitting machine

<u>Mean</u>	<u>Variance</u>
$\bar{Z}_1 = - 0.17$	$S_1^2 = 0.56$
$\bar{Z}_2 = - 0.22$	$S_2^2 = 0.74$
$\bar{Z}_3 = - 0.32$	$S_3^2 = 0.71$
$\bar{Z}_4 = - 0.30$	$S_4^2 = 0.55$
$\bar{Z}_5 = + 0.09$	$S_5^2 = 0.92$
$\bar{Z}_6 = + 0.91$	$S_6^2 = 0.53$

N = 35.

A number of tests were conducted to examine for bias amongst this data. Firstly, the largest and smallest variances,  $S_5^2$  and  $S_6^2$ , were subjected to an F test. The ratio, 1.74, is less than the critical value at the 95% confidence level with 34 and 34 degrees of freedom ( $F_c = 1.77$ ). Therefore, Till's (1974, p.61) method of applying a t test to means can be applied to any pair of means in this data. A mean,  $\bar{Z}$ , of zero would imply that the container in question had received exactly a sixth of each sample load passing through the hopper. Therefore  $\bar{Z}_5$  is taken to represent the closest approach to the ideal. Testing  $\bar{Z}_3$  against  $\bar{Z}_5$  will establish if the largest negative bias is significant, and testing  $\bar{Z}_6$  against  $\bar{Z}_5$  will establish the significance of the largest positive bias, (see Table 4.10).

Table 4.10 Tests for significance of difference in means for standardised data from splitting machine.

<u>Pair tested</u>	<u>Sp</u>	<u>t</u>	<u>Result</u>	
$\bar{Z}_3$ & $\bar{Z}_5$	0.92	1.86	NS	at 95%
$\bar{Z}_6$ & $\bar{Z}_5$	0.86	3.99	SIG	at 99%

For explanation of abbreviations see Table 4.6.

The tests show that container 6 received significantly more material each time than it should, whilst this positive bias was counteracted by a spread of deficiencies, all not significant, in containers, 1,2,3 and 4. No reason for this bias in favour of container 6 is evident from an examination of the machine, but it may be counteracted by randomising the containers relative, both to each other, and to the revolving base of the machine.

#### 4.3.3. The influence of sieving

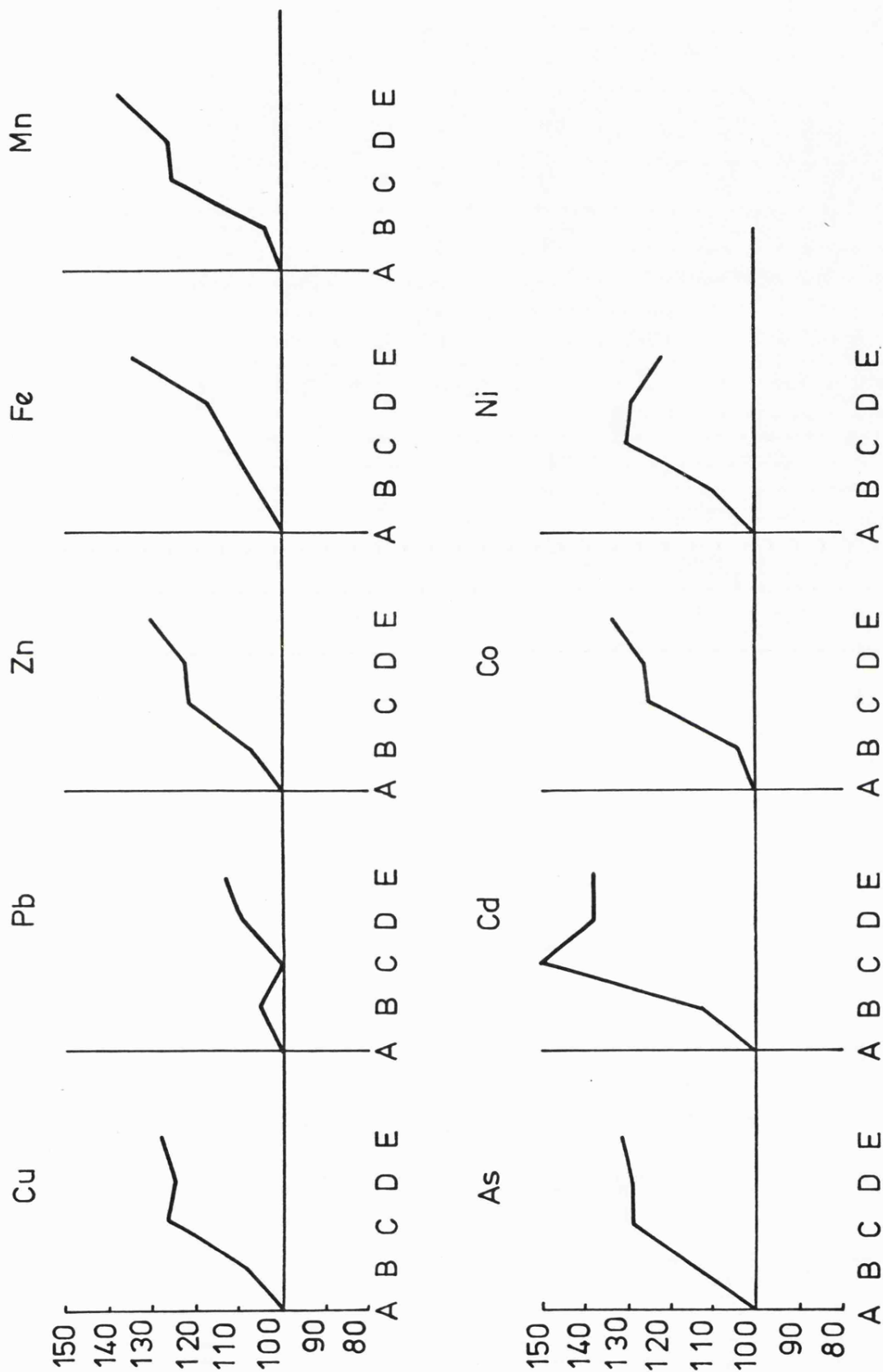
##### 4.3.3.1. Introduction.

Mention was made in Section 4.3.1. that material passing a 190 micron sieve, 2 to 3 minutes after the start of mechanical sieving, is predominantly of coarse grain size (i.e. just less than 190 microns). This leads to the intuitive conclusion that, in the case of base and associated metals, the material first passing the sieve will be more metal-rich than material passing later.

##### 4.3.3.2. Experiments

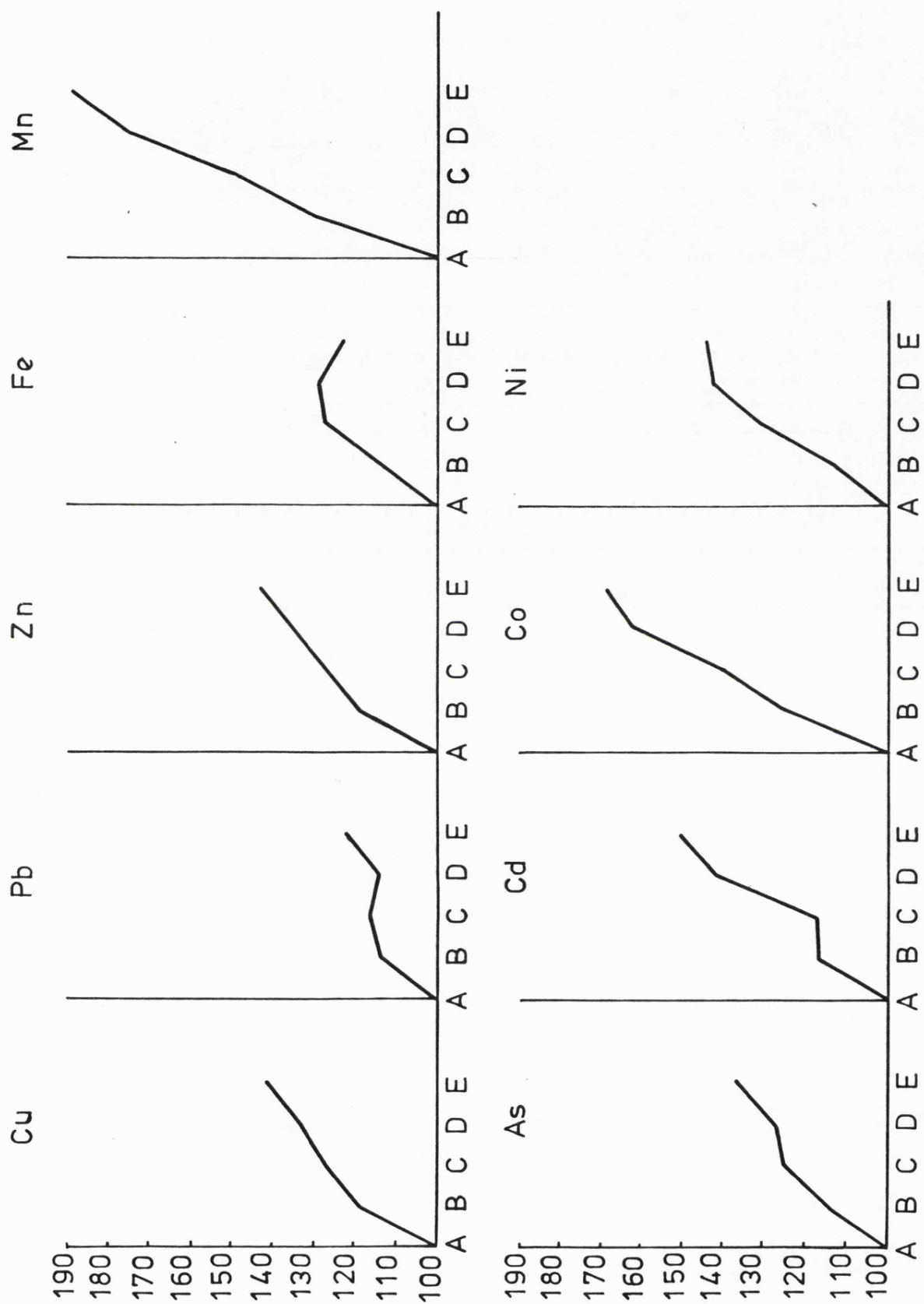
Five sediment samples, collected at localities Yw 124 to 128 inclusive, in the Pottery Leat at Yarner Wood, between 27870787 and 27830784 (see Fig. 1.2 ), were sieved at 125 microns by hand, in such a way that, as well as producing a composite sample, portions of sample passing the sieve at various time intervals were also isolated. The samples, A to E inclusive, represent the material passing between 0 and 10s, 10 and 20s, 20 and 30s, 30 and 40s and 40 and 60s. Analysis by AAS for Cu, Pb, Zn, Fe, Mn, As, Cd, Co and Ni followed a 4-hour digestion in 4M HNO<sub>3</sub>.

The results are shown in Figures 4.2 to 4.6, and have been calculated so that the value for sample A (0 to 20s) is set to 100% and the other samples (B to E inc.) are expressed as percentages of A.



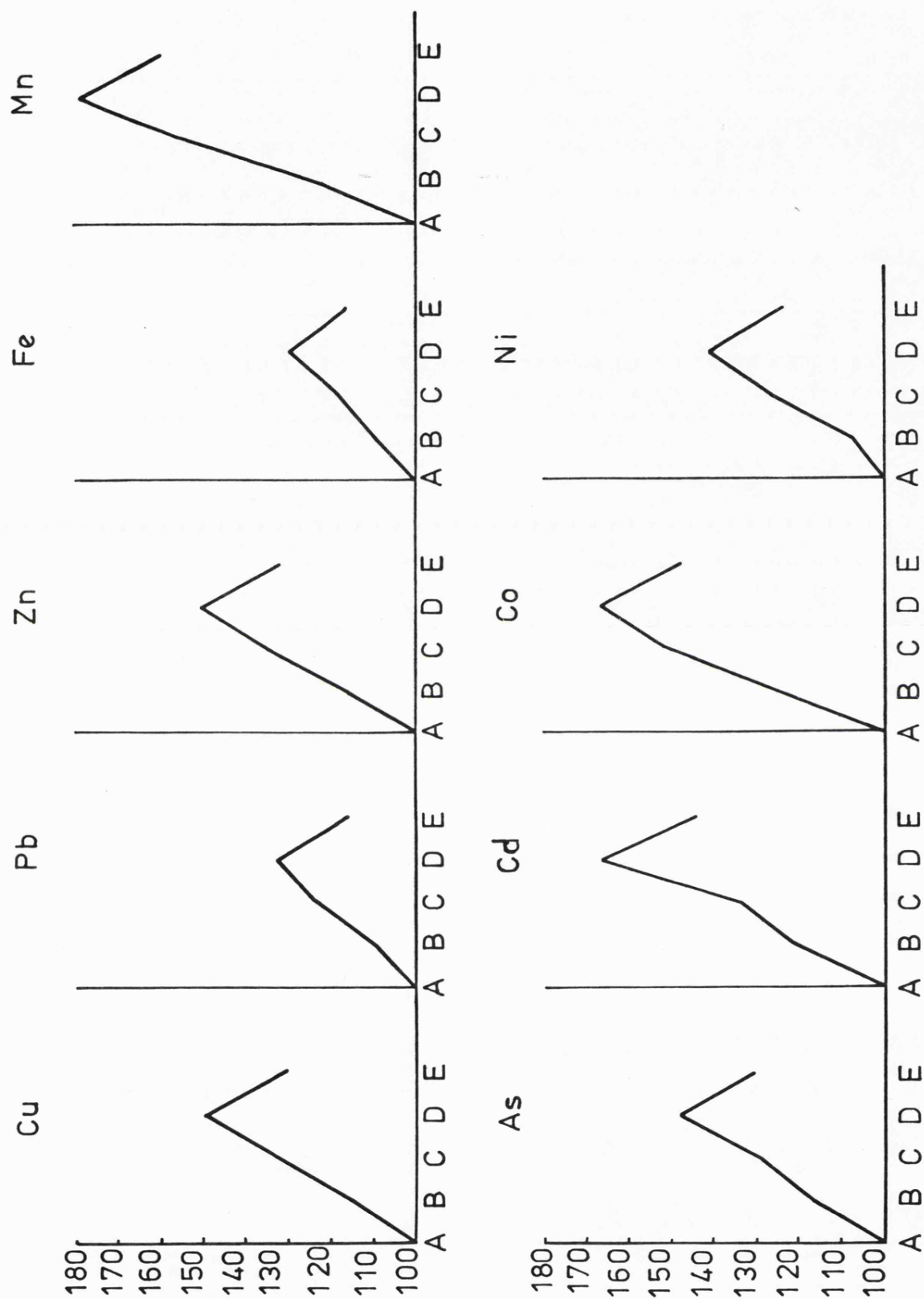
Sample Yw 124a. Sample A set to 100%, other samples expressed as % age of A  
 A, 0 - 10s; B, 10 - 20s; C, 20 - 30s; D, 30 - 40s; E 40 - 60s.

FIG. 4.2 INFLUENCE OF TIME ON METAL CONTENT OF MATERIAL PASSING SIEVE. SAMPLE Yw 124a



Sample Yw 125a Legend as for Fig 4.2

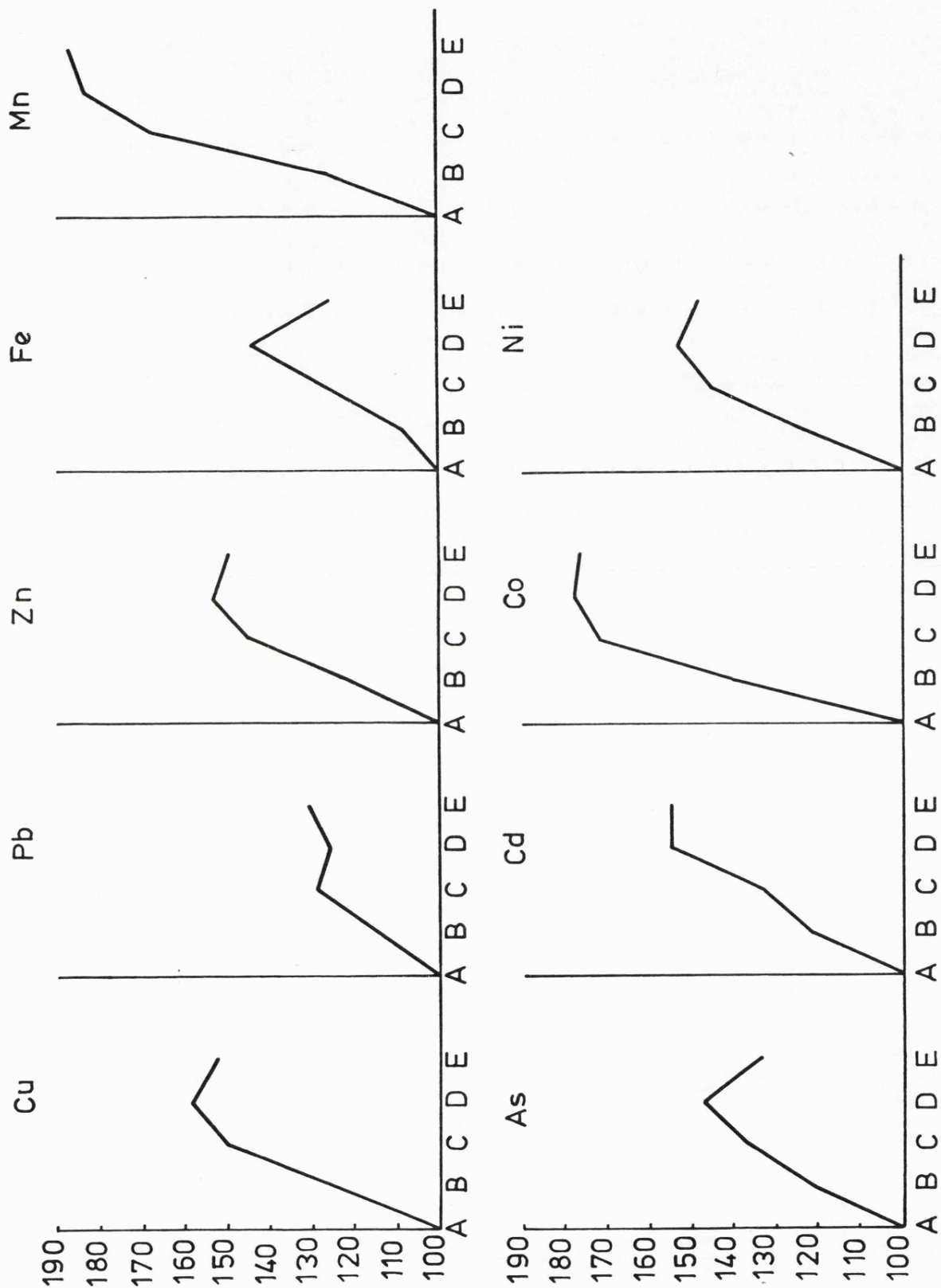
FIG. 4. 3 INFLUENCE OF TIME ON METAL CONTENT OF MATERIAL PASSING SIEVE. SAMPLE Yw 125a.



Sample Yw 126a Legend as for Fig 4.2

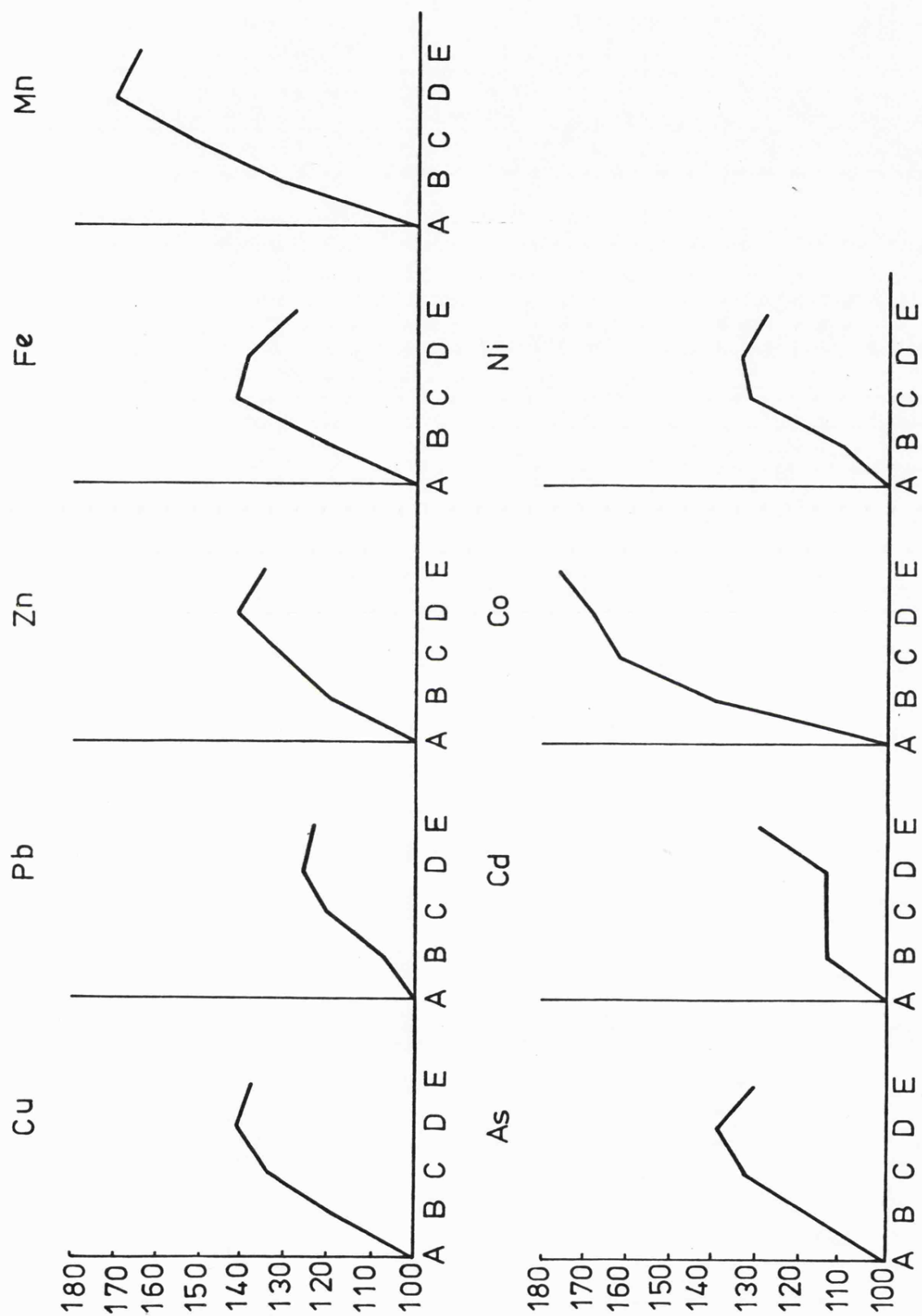
**FIG. 4.4** INFLUENCE OF TIME ON METAL CONTENT OF MATERIAL PASSING SIEVE. SAMPLE Yw 126a





Sample Yw 127a Legend as for Fig 4.2

FIG. 4.5 INFLUENCE OF TIME ON METAL CONTENT OF MATERIAL PASSING SIEVE. SAMPLE Yw 127a.



Sample Yw 128a Legend as for Fig 4.2

FIG. 4.6 INFLUENCE OF TIME ON METAL CONTENT OF MATERIAL PASSING SIEVE. SAMPLE Yw 128a

The graphs show that none of the values falls below 100% and that a maximum of 188% is reached by sample Yw 125a/E for Mn (Fig. 4.3). It must therefore be concluded that, far from the smallest, most metal-rich particles coming through the sieve first, the most metal-rich material comes through considerably later. However, 32 of the 45 graphs in Figures 4.2 to 4.6 show either a decrease below their maximum towards the end of the sieving period, or at least a marked slackening of gradient. It may, therefore, be argued that the barren material anticipated during the latter stages of sieving might have been observed had the experiment gone on longer.

What is apparent is that the most metal-rich material seems to pass the sieve between 30 and 60 seconds after sieving begins. Further, if it is assumed that the metal-rich, fine grained material normally present in a sample, falls through the sieve most easily, it is necessary to postulate some extra source of metal-rich material, the bulk of which passes the sieve between 30 and 60 seconds.

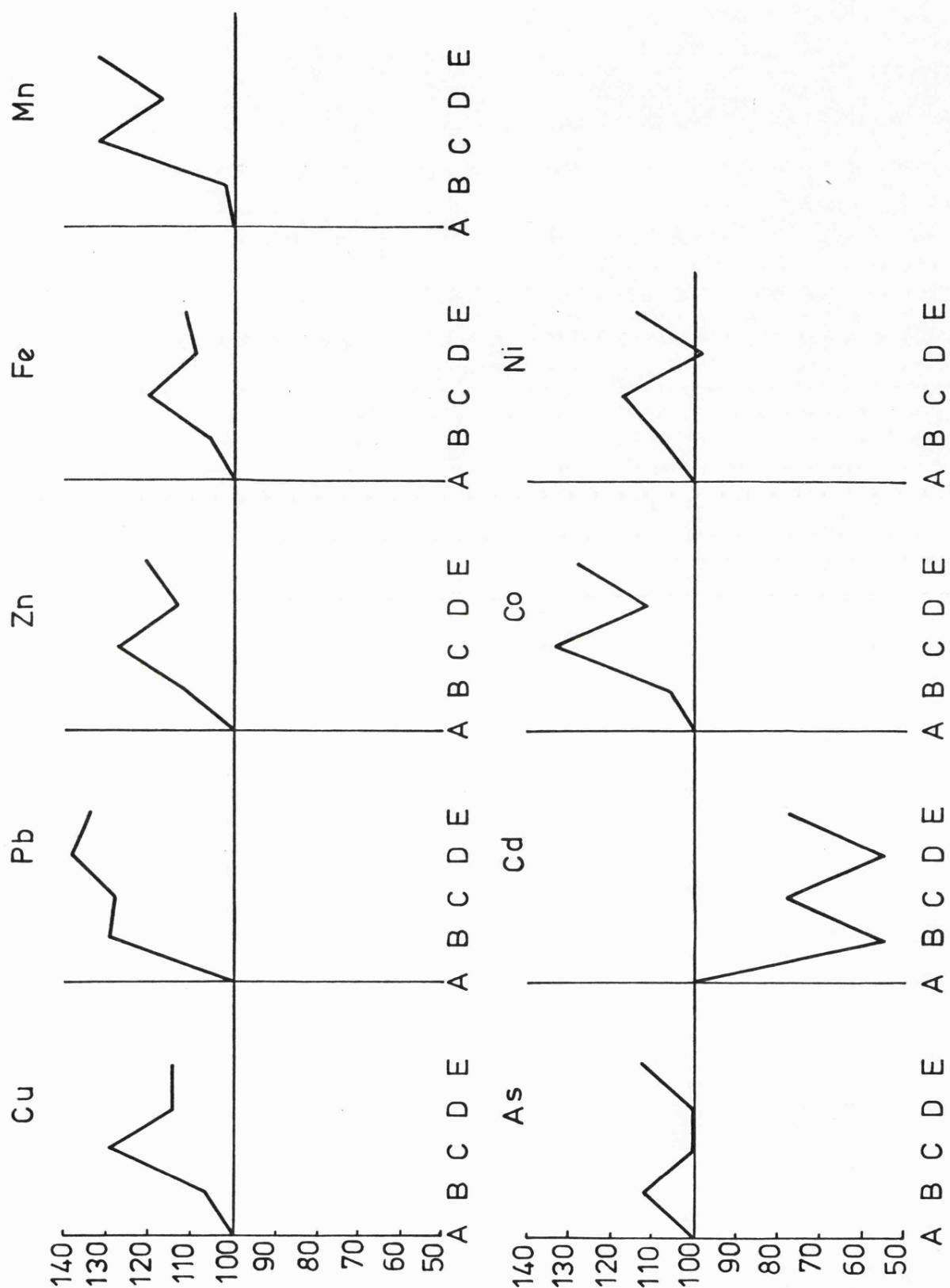
Horsnail and Elliot (1971), Plant (1971), Loganathan and Burau (1973) and Whitney (1975) are amongst the numerous authors who have, in recent years, pointed out the metal-rich nature of Fe and Mn oxide/hydroxide coatings on particles in stream sediments. Visual examination of the present samples revealed that Fe and Mn coatings are present, and one possible explanation for the increase in metal, as sieving proceeds, is that metal-rich coatings are abraded from the coarser grains as they grind together in the sieve. Co and Zn mirror the distribution of Mn particularly well and interaction of Fe with Mn could explain the distribution of most of the elements in Figures 4.2 to 4.6, with Fig. 4.4 being the most striking example.

Further examination of this phenomenon was effected with the collection of five samples in the River Mardle, and one of its tributaries, draining the old copper mines at Brookwood, near Buckfast (see Fig.1.3 ). The samples, SV1-5 inclusive, were treated and analysed as described above and the results are shown in Figures 4.7 to 4.11 inclusive. This section of stream was selected because it is known to be high in base metal, draining extensive old mine workings, but it is much less pronouncedly Fe and Mn oxide/hydroxide stained than the Pottery Leat tributary of Yarner Stream, from which Yw 124a - 128a were collected.

The results show a mixture of positive and negative values and only sample SV 4 shows the strong upward trend, so obvious in the material from Yarner Wood. A pronounced negative trend is observed in SV 3 for Cu and As, as was initially predicted by intuition, and the relatively stable distribution of Fe and Mn in this sample (maximum deviation + 18%) implies that even if coatings are present, (and they have not been observed), they are not being abraded. In contrast, sample SV 4 does show a positive relationship between sieving time and trace metal content. Furthermore, the Fe and Mn distribution in this sample implies that coatings may well be present, although they are not apparent to visual examination.

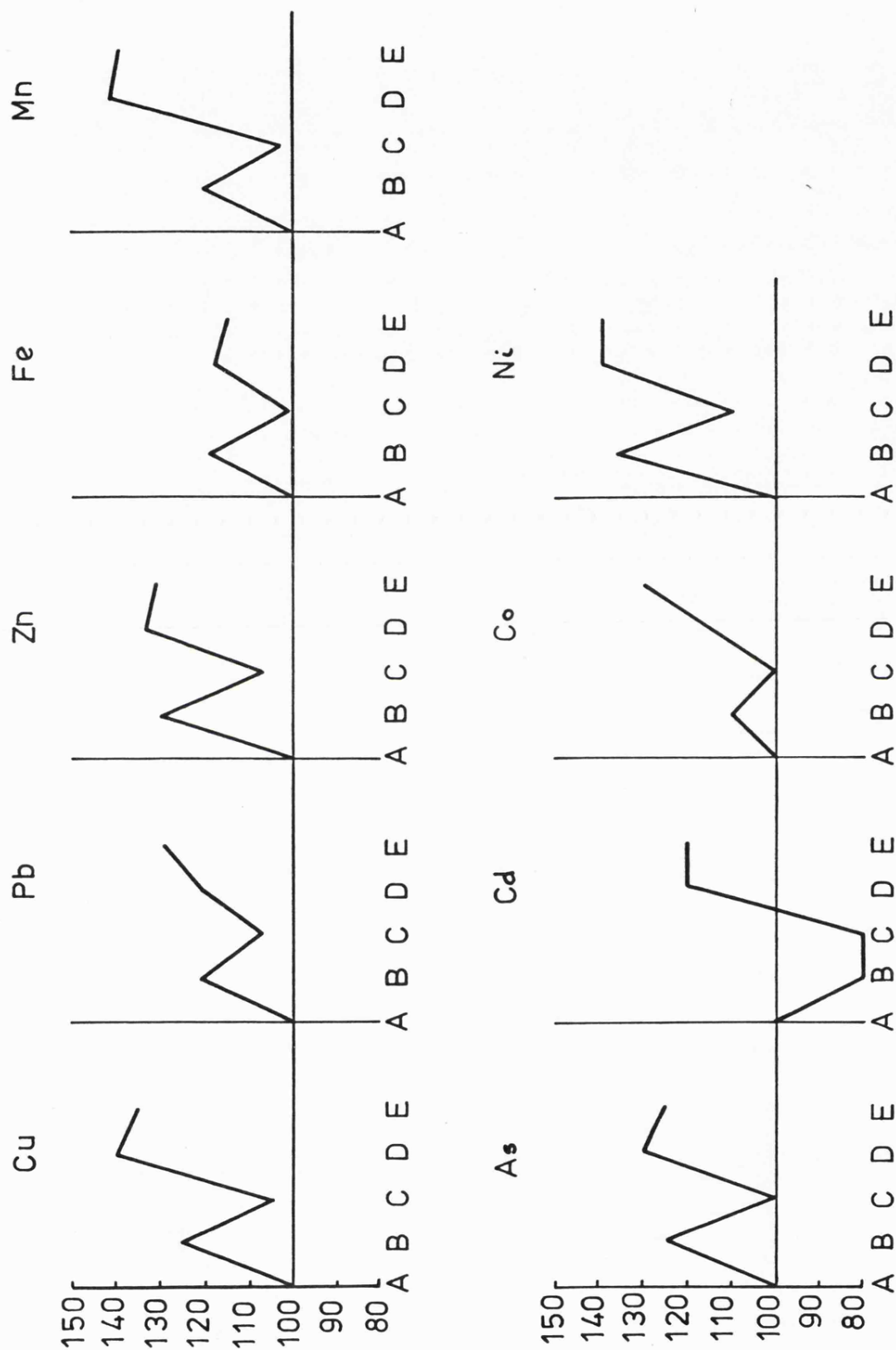
#### 4.3.3.3. Conclusions

Although it might be expected that the finest grained, most metal-rich material should pass the sieve quickly, subsequently giving rise to progressively more metal-poor material, the presence of metal-rich Fe and Mn oxide/hydroxide coatings, which may abrade from large grains as sieving progresses, can complicate the picture.



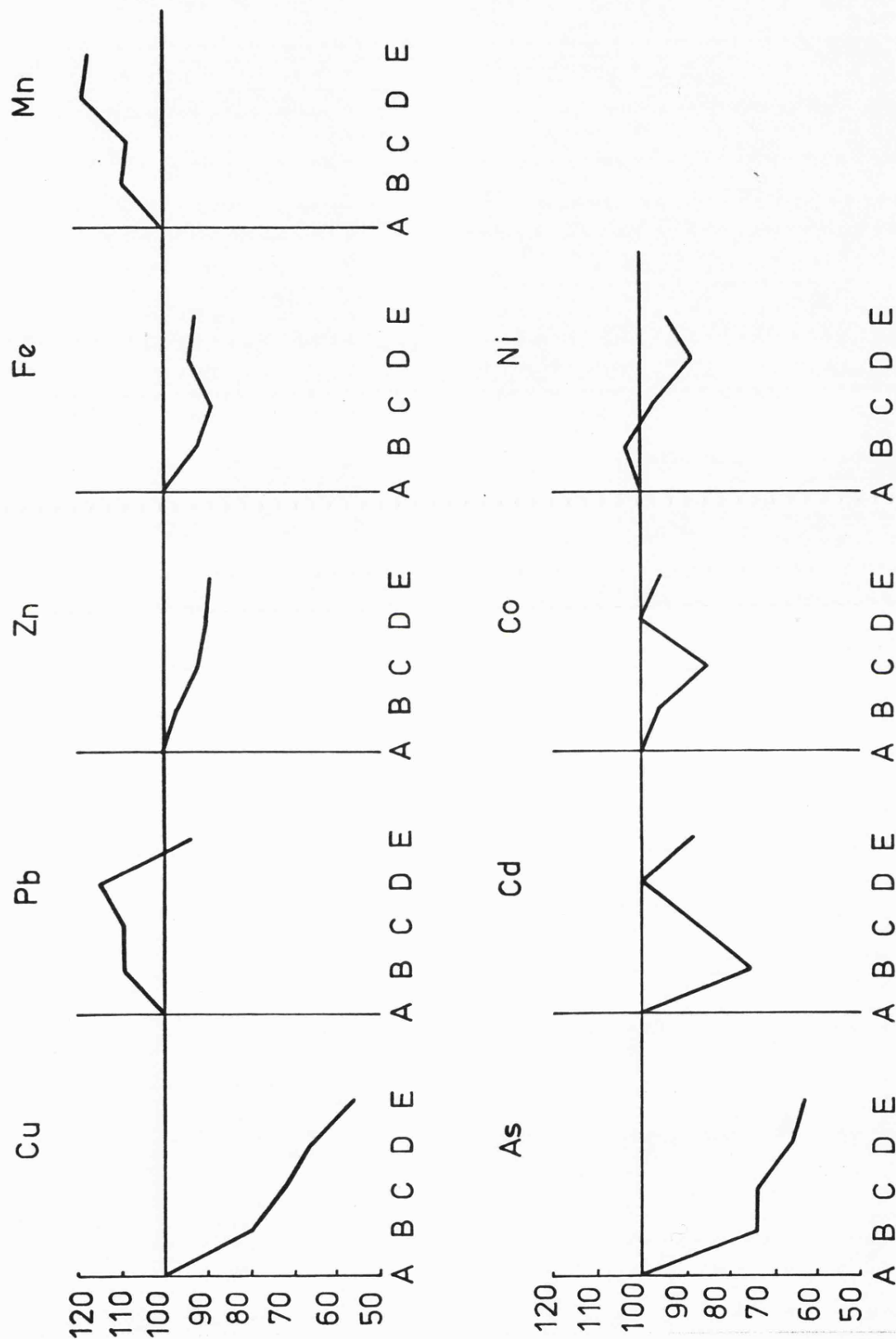
Sample SV1 Legend as for Fig 4.2

FIG. 4.7 INFLUENCE OF TIME ON METAL CONTENT OF MATERIAL PASSING SIEVE. SAMPLE SV1



Sample SV2 Legend as for Fig 4.2

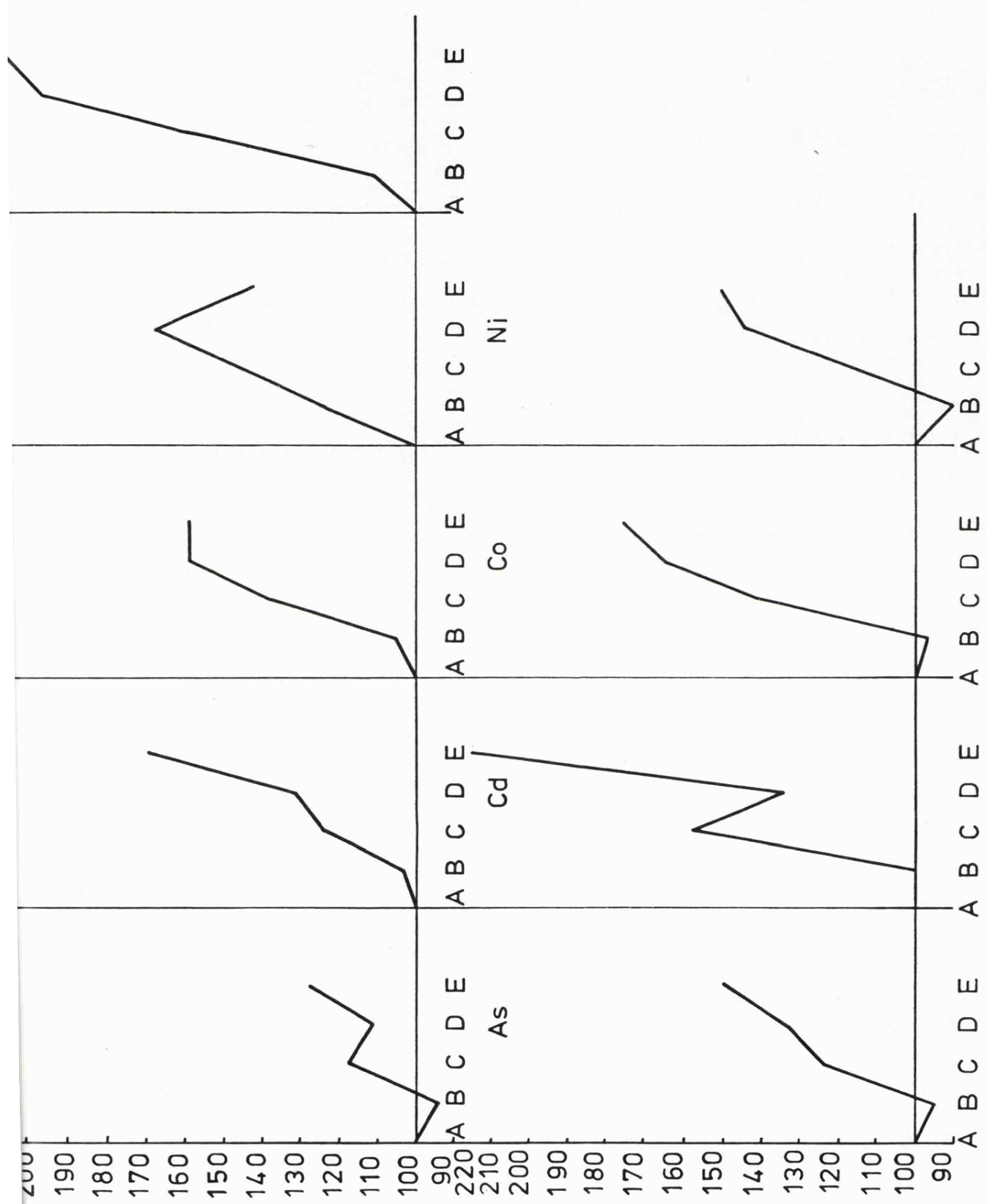
FIG. 4.8 INFLUENCE OF TIME ON METAL CONTENT OF MATERIAL PASSING SIEVE. SAMPLE SV 2.



Sample SV3 Legend as for Fig. 4.2

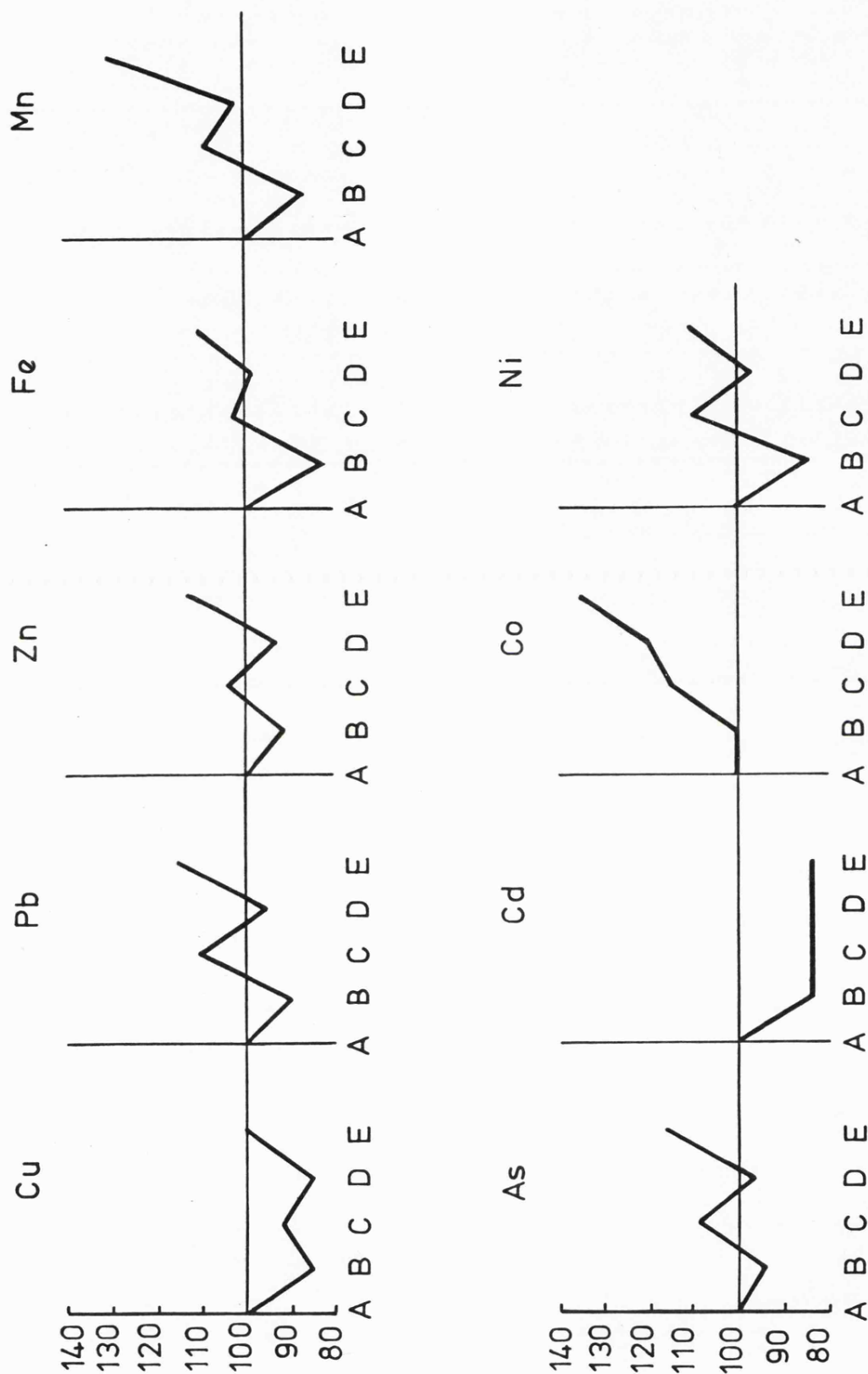
FIG. 4.9 INFLUENCE OF TIME ON METAL CONTENT OF MATERIAL PASSING SIEVE. SAMPLE SV3

4.10 INFLUENCE OF TIME ON METAL CONTENT OF MATERIAL  
PASSING SIEVE. SAMPLE SV4



Sample SV4 Legend as for Fig. 4.2





Sample SV5 Legend as for Fig.4.2

FIG. 4.11 INFLUENCE OF TIME ON METAL CONTENT OF MATERIAL PASSING SIEVE. SAMPLE SV5

Further examination of this phenomenon was effected with the collection of five samples in the River Mardle, and one of its tributaries, draining the old copper mines at Brookwood, near Buckfast (see Fig.1.3 ). The samples, SV1-5 inclusive, were treated and analysed as described above and the results are shown in Figures 4.7 to 4.11 inclusive. This section of stream was selected because it is known to be high in base metal, draining extensive old mine workings, but it is much less pronouncedly Fe and Mn oxide/hydroxide stained than the Pottery Leat tributary of Yarner Stream, from which Yw 124a - 128a were collected.

The results show a mixture of positive and negative values and only sample SV 4 shows the strong upward trend, so obvious in the material from Yarner Wood. A pronounced negative trend is observed in SV 3 for Cu and As, as was initially predicted by intuition, and the relatively stable distribution of Fe and Mn in this sample (maximum deviation + 18%) implies that even if coatings are present, (and they have not been observed), they are not being abraded. In contrast, sample SV 4 does show a positive relationship between sieving time and trace metal content. Furthermore, the Fe and Mn distribution in this sample implies that coatings may well be present, although they are not apparent to visual examination.

#### 4.3.3.3. Conclusions

Although it might be expected that the finest grained, most metal-rich material should pass the sieve quickly, subsequently giving rise to progressively more metal-poor material, the presence of metal-rich Fe and Mn oxide/hydroxide coatings, which may abrade from large grains as sieving progresses, can complicate the picture.

Assuming that Fe and Mn coatings are responsible for this effect, it would be minimised if the samples were to be given a light crushing to liberate the coatings before sieving. The effect of such a crushing, to reduce sample variability, was noted in the past (i.e. Plant, 1971), although the reason for this decrease was usually attributed to reduction in sample grain size. Unfortunately, by the time the present experimental work was complete, all the material collected in the field had been sieved, and it was not, therefore possible to confirm this suggestion experimentally.

The fact that such pronounced fluctuations do occur suggests that attempts to improve reproducibility may benefit from a mechanical, systematic sieving procedure in any event, and further highlights the pitfalls of comparing one set of survey data with another, especially when sample preparation techniques have not been fully described.

#### 4.4 SUB-SAMPLING

An attempt was made to determine whether or not the method of removing material from a sample bag is critical, and also to see whether rhythmic vibration for 15 hours causes any detectable settling in sample packets. The author's interest in this latter problem was aroused by the necessity in some parts of the world to air-freight samples for analysis. It seems likely that, if settling has taken place within the sample packet, the common practice of scooping from the top of the material in the packet may introduce a bias. Therefore, as a matter of routine in the current work, each packet was emptied onto a piece of glossy paper, and sub-samples removed from one quarter of the resultant cone.

By way of comparison, each of one batch of 40 samples from Yarner Wood were sub-sampled by both methods and the results compared. Although no machine capable of reproducing in-flight vibration was available to the

author, 10 samples were set on an orbital shaker for 15 hours at 150 rpm and then sub-sampled off the top of the material in the packet. Analysis by AAS for Cu, Pb, Zn, Mn, As, Cd, Co and Ni followed a 4 hour digestion in 4M  $\text{HNO}_3$ . Moroney (1953, p.228) adapts the t test to two sets of analyses of the same group of samples, by calculating the mean and standard deviation of the discrepancies between the two estimates for each sample. Tables 4.11 and 4.12 summarise these tests applied to the current investigation.

Sub-sampling directly from the packet only caused a significant discrepancy for Pb and the period of 15 hours on the orbital shaker caused no significant discrepancies. However, the long period, horizontal movements of an orbital shaker do not closely resemble aircraft vibrations which tend to be short period, high-frequency movements, and so a case can still be made for the need to homogenise samples after airfreighting. The fact that, even for only one element, a significant discrepancy was detected between the two sub-sampling techniques, means that one technique or the other should be adopted as standard, and because pouring the sample out offers a better chance of homogenising the material, its adoption may be justified, despite the slight extra time taken in so doing.

#### 4.5 CONCLUSIONS

Sample preparation is an area of Applied Geochemistry which, probably more than any other, is subject to traditional and "rule of thumb" techniques. A number of aspects have been investigated, and a case can now be made for the necessity of drying samples thoroughly as soon as possible after collection. Failure to do so causes erratic alteration in metal content, especially for Fe and Mn, but also to a

**TABLE 4.11** Results of comparison between sub-sampling after emptying packet and from within packet

<u>Element</u>	<u><math>\bar{D}</math></u>	<u><math>S_D</math></u>	<u>N</u>	<u>t</u>	<u>Result</u>
Cu	- 1.0	16.84	40	0.37	NS
Pb	- 4.38	10.00	40	2.74	SIG
Zn	- 5.0	30.17	39	1.02	NS
Mn	-18.75	316.9	40	0.37	NS
As	+28.5	152.3	40	1.17	NS
Cd	- 0.13	0.48	40	1.69	NS
Co	+ 0.73	4.17	40	1.09	NS
Ni	0.0	6.89	40	0.00	NS

Critical t value for two-tailed test  $\alpha = 0.05$ , with 39 degrees of freedom is 2.02.

$\bar{D}$  denotes mean discrepancy

$S_D$  denotes Standard deviation of discrepancies

N denotes number of pairs compared

t denotes student's t.

NS denotes difference not significant at  $\alpha = 0.05$

SIG denotes difference is significant at  $\alpha = 0.05$ .

**TABLE 4.12** Comparison between sub-sampling off top of packet before and after 15 hours on orbital shaker.

<u>Element</u>	<u><math>\bar{D}</math></u>	<u><math>S_D</math></u>	<u>N</u>	<u>t</u>	<u>Result</u>
Cu	+ 1.0	20.39	10	0.15	NS
Pb	- 5.0	9.08	10	1.65	NS
Zn	+ 5.5	26.61	10	0.62	NS
Mn	+24.0	262.8	10	0.27	NS
As	-16.0	125.0	10	0.38	NS
Cd	- 0.15	0.47	10	0.96	NS
Co	+ 0.4	4.60	10	0.26	NS
Ni	+ 0.5	7.01	10	0.21	NS

Critical t value is 2.26

Legend as for Table 4.11.

lesser extent for Zn. This may be due to water trapped between grains causing dissolution and removal and/or re-deposition of Mn and Fe oxides and hydroxides.

Drying samples at temperatures in excess of 80°C may be desirable from the point of view of speed but at 150°C significant changes in sample chemistry were observed for some elements and when temperatures as high as 500°C were used, very significant changes occurred. A more detailed investigation, within the range 70°C - 150°C, might prove useful, although the ignition point of the paper used for sample bags may prove to be a significant controlling factor.

Use of a mechanical shaker results in a systematic sieving action, and a two minute shaking period appears to be adequate for the removal of most of the minus mesh fraction. Data presented shows the grain-size composition of five bulk samples, which confirms the bimodality of stream sediment material, peaks occurring within the minus 2 mm plus 190 micron and the minus 125 micron ranges.

When necessary, sample material was divided up using a Pascal Rotating Sample splitter. Data was prepared to show that a slight systematic bias is present in this machine and to overcome this, the sample buckets should be arranged in random order relative to each other and to the rotating base plate of the machine.

Variations in the chemistry of material passing a 125 micron sieve at various times after the commencement of sieving were observed. Samples from Yarner Wood, where Mn and Fe oxide staining is prominent in the stream, showed a pronounced upwards trend in all metals up to about 60 seconds sieving time. Similar trends were only present in one of five samples collected in the Brookwood area where Mn and Fe staining is largely absent. It is, therefore, proposed that the observed

increases in metal content may be due to the abrading of metal rich Mn and Fe oxide/hydroxide coatings off larger particles grinding together as sieving progresses. This again highlights the need for standardised, prolonged sieving of samples if reproducibility is to be achieved. Further work might investigate the suggestion that the increase in reproducibility brought about by light crushing of samples (Plant, 1971), prior to sieving, may be due to the liberating of coatings.

Finally, two methods of removing material from sample packets were compared. Scooping straight from the material in the packet only produced a significantly different result from sampling after pouring out all the material, for one element, Pb. Fifteen hours on an orbital shaker was found to make no significant difference to the results obtained from scooping material out of the packet. However, more intense vibrations, such as would be experienced in an aircraft, may well cause a greater degree of settling. Therefore, pouring out samples onto a sheet of paper to homogenise them before sub-sampling, seems to be good practice and is only marginally more time-consuming.

## CHAPTER 5

### VARIABILITY INTRODUCED DURING ANALYTICAL PROCEDURES

#### 5.1. INTRODUCTION

#### 5.2. DIRECT VARIABILITY

##### 5.2.1. Instrumental variability

##### 5.2.2. Variability between batches and standards

###### 5.2.2.1. Variability between batches

###### 5.2.2.2. Comparison of the dilute standards.

#### 5.3. VARIABILITY CAUSED BY CHANGES IN TECHNIQUE

##### 5.3.1. Acid leach storage before analysis

##### 5.3.2. Reading obtained as a function of sample weight

###### 5.3.2.1. Outline of problem

###### 5.3.2.2. Balances check

###### 5.3.2.3. Settling temperature

###### 5.3.2.4. Alternative analytical configurations

###### 5.3.2.5. Rigour of attack

###### 5.3.2.6. Extent of dilution

###### 5.3.2.7. Interferences

###### 5.3.2.8. Standards

###### 5.3.2.9. Conclusions

##### 5.3.3. Determination of arsenic

###### 5.3.3.1. Introduction

###### 5.3.3.2. Comparison with other techniques

###### 5.3.3.3. Chemical nature of As at Yarner Wood

###### 5.3.3.4. Conclusions



#### 5.3.4. Spectral interferences between Ag and Cu

##### 5.3.4.1. Introduction

##### 5.3.4.2. Examination of Ag analytical procedure

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#### 5.3.5. Determination of Sn

##### 5.3.5.1. Introduction

##### 5.3.5.2. Atomic absorption spectrophotometry

##### 5.3.5.3. Concentration and sample weight

##### 5.3.5.4. Conclusions

#### 5.4. CONCLUSIONS

## CHAPTER 5

### VARIABILITY INTRODUCED DURING ANALYTICAL PROCEDURES

#### 5.1. INTRODUCTION

The sources of variability discussed in this Chapter may be divided into two types; direct and indirect. Direct variability concerns the reproducibility of the analytical method in use, be it an atomic absorption spectrophotometer, or the human eye in conjunction with a colorimetric technique. In this instance it includes instrumental drift and reading error for AAS and also includes loss of reproducibility between batches of samples, brought about by changes in standard solutions used for calibration.

Indirect variability concerns changes in analytical technique which can cause poor reproducibility, even in the absence of direct variability, and some potential sources have been investigated. A series of experiments was undertaken to determine how long samples may be left after digestion, without loss of analytical quality. The experiments on sub-sample optimisation described in Chapter 2, produced an unexpected result, in that as greater weights of a sample were taken for analysis, the result obtained was found to decrease. A number of possible explanations of this phenomenon, mostly related to changes in technique, were examined. However, the final explanation may lie in the realms of atomic absorption interference, which should, perhaps, be more correctly assigned to direct variability.

Arsenic was shown to be a very good indicator of mineralisation in the Yarner Wood area (see Chapter 8) and more widely in South Devon (C.H. James, personal communication). The use of 4M nitric acid as a digesting agent has resulted in high levels of As being reported, and comparisons with various other techniques for As determination are presented, as well as evidence for the chemical form in which the As is present.

Examination of the close correlation between Cu and Ag observed throughout this study has resulted in the discovery of a spectral interference when using a Ag-Cu-Cr-Ni multi-element lamp for the AAS determination of Ag, and methods of overcoming this problem are discussed.

Some aspects of analysis for Sn were also examined. AAS determination of Sn using an air/acetylene flame, following an ammonium iodide digestion, has proved successful and a considerable time-saver over colorimetry. However, the efficiency of the ammonium iodide attack is seriously questioned as the weight of sub-sample taken for analysis appears to influence the final result.

## 5.2. DIRECT VARIABILITY

### 5.2.1. Instrumental variability

As a matter of routine, throughout these investigations, checks for instrumental drift and error were applied. Blank solutions were composed of 0.5% lanthanum chloride in 10% nitric acid, in de-ionised water. Standard solutions were also made up in nitric acid, to maintain a low pH and prevent metal precipitation onto the walls of glass containers used for storage. The method of sample reading adopted, involved the aspiration of a blank, a maximum standard (set to 100 units of instrument scale) and at least one intermediate standard. In addition, as a control on precision, for every ten routine samples read, a repeat reading was made of one of the ten. In this way, any differences between standards and their correct values due to poor adjustment of the instrument (or to drift during the routine readings) could be allowed for. Having made adjustments for drift, any remaining discrepancy between the routine reading, and its repeat in a set of 10, is due to instrumental error. Table 5.1 shows the levels of instrumental error for nine elements in Yarner Wood samples and also the proportion of the total error that it represents.

**TABLE 5.1** Level of Instrumental Error from Yarner Wood samples and proportion of total error (data  $\log_{10}$  transformed).

	Cu	Pb	Zn	Fe	Mn	As	Cd	Co	Ni
Variance ( $\times 10^{-4}$ )	1.49	1.55	3.55	2.21	1.01	2.87	36.4	1.65	5.60
% of total error	8.4	9.7	11.1	6.1	0.7	7.4	86.5	3.4	16.9

The instrumental errors for each element are of similar magnitude and less than 20% of total error for all elements except Cd, for which most of the samples are close to the detection limit. For Cd, a small discrepancy, in terms of scale units on the instrument, constitutes a large proportion of the concentration of the original. This explains both the high absolute value of the analytical variance for Cd, and also the fact that such a high proportion of total error variance can be attributed to the analytical variance (see Chapter 3, Table 3.3).

#### 5.2.2. Variability between batches and standards

##### 5.2.2.1. Variability between batches

It was suggested by Barr and Hawkes (1963) that samples left in sample packets may "age" and, if re-analysed after lengthy storage, not necessarily give results comparable with analysis close to the time of collection. A set of 30 samples from Yarner Wood were first analysed for Cu, Pb, Zn, Fe and Mn during the first week in July 1977 and for As, Cd, Co and Ni in the third week of October 1977. They were repeated for all nine elements on the 8th May 1978, 10 months after the first set of analyses and six and a half months after the second.

The results for the two batches were compared by recourse to the mean and variance of the discrepancies (Moroney, 1953, p.228) and Table 5.2 summarizes the results of these tests. Between-batch discrepancies are only significant for Fe, Mn and Co, contrary to the findings of Barr and Hawkes (op.cit.) who found a 10% reduction in Cu after six months.

TABLE 5.2 Evaluation of between-batch discrepancies

Element	$\bar{R}$ (ppm)	$\bar{D}$	$S_D$	t	Result
Cu	360	+4.23	47.8	0.49	NS
Pb	54	-0.90	3.19	1.55	NS
Zn	257	+8.33	41.3	1.10	NS
Fe	45,730	-4576	6023	4.15	SIG
Mn	3,340	-1300	1975	3.36	SIG
As	1,997	+0.50	153.1	0.02	NS
Cd	3.1	+0.10	0.36	1.51	NS
Co	54	+3.6	6.11	3.23	SIG
Ni	67	-1.50	6.52	1.26	NS

$\bar{R}$  denotes mean reading

$\bar{D}$  denotes mean discrepancy

$S_D$  denotes standard deviation of discrepancies.

t denotes Student's t values  $t = \frac{\bar{D}\sqrt{n}}{S_D}$

NS denotes discrepancy not significantly different from zero, at 95% confidence level.

SIG denotes discrepancy significantly different from zero at 95% confidence level.

New 1000  $\mu\text{g/ml}$  stock solutions for Mn and Fe were made between the dates of the two sets of analyses. In the case of Mn, however, the new solution was prepared during the analysis of another set of samples, and the fact that the new stock was not the same strength as the old, was proved at that time. In the case of Fe, no such evidence is available

even though new stock solutions had been prepared between the given dates. No change in Co stock solutions had been made over the period and it is not possible to postulate an alternative cause for this significant variation.

In conclusion, ageing has not been observed for Cu, Pb and Zn in samples left for 10 months, nor for As, Cd and Ni in samples left for six and a half months. Apparent differences in the Mn content are definitely attributable to a change in stock solution, and a similar explanation is suggested for Fe. However, no such explanation can be offered for Co. The majority of the evidence of this study finds against ageing of samples, but it does highlight the fact that, even if significant between-batch variations are observed, it should not be overlooked that changes in standard solutions, or other variations in analytical conditions, may be responsible for the differences rather than changes in the samples themselves.

#### 5.2.2.2. Comparison of dilute standards.

Dilute standards, containing 2  $\mu\text{g/ml}$  Cu, 10  $\mu\text{g/ml}$  Pb and 1  $\mu\text{g/ml}$  Zn, were made up with 2%  $\text{HNO}_3$  and stored. They were re-read after various time intervals and compared with freshly made standards of the same strength.

Till's (1974,p.61) method of testing differences between means was adopted and the results summarised in Table 5.3. These indicate that dilute standards show no observable variations after one week's storage, in the case of Pb, or three weeks storage in the cases of Cu and Zn. Dilute standards for AAS work are seldom made in quantities larger than 100 ml, and during continual analytical work such a small quantity will be used quickly. Significant variations due to

deterioration of standards are therefore considered unlikely in normal usage.

TABLE 5.3: Comparison of dilute standards stored for various periods of time, with similar standards, freshly made.

Element	Storage period	t value	Result
Cu	1 day	1.37	NS
Cu	7 days	0.21	NS
Cu	21 days	1.02	NS
Pb	1 day	1.61	NS
Pb	2 days	2.09	NS
Pb	7 days	0.94	NS
Zn	1 day	1.29	NS
Zn	2 days	0.75	NS
Zn	3 days	2.15	NS
Zn	7 days	0.35	NS
Zn	21 days	1.66	NS

NS denotes difference in means not significant at 95% confidence level.

t calculated according to Till (1974, p.61).

### 5.3 VARIABILITY CAUSED BY CHANGES IN TECHNIQUE

#### 5.3.1. Acid leach storage before analysis

It is frequently impracticable to analyse a sample for all elements of interest immediately following digestion, and so a number of alternative storage methods were tried. These included storage after dilution and decanting into 10 ml sample cups, after dilution, but before decanting, and storage before dilution. Some samples were left for up to 11 days before analysis. Decanting samples into 10 ml cups was considered to be good practice, as it separates liquid from solid and thus prevents solid material being aspirated and clogging the nebuliser input tube.

The results obtained from analysis of these samples lend themselves to the classical 2-way analysis of variance model. The computer programme given by Davis (1973, p.115) for 2-way analysis of variance has been modified to operate on  $\log_{10}$  transformed data, and also to incorporate the calculation of Fisher's Least Significant Difference statistic (see Till, 1974, p.111). The final programme and a specimen output are presented in Appendix 2.

The sample material and analytical conditions used during this experiment were deliberately set to reproduce standard practice in a commercial situation. 0.2g of minus 190 micron material was digested for 4 hours in 4M  $\text{HNO}_3$  at 95°C and diluted to 10 ml with de-ionised water. Nine batches of 20 such samples were subjected to the various treatments outlined below.

The first set of comparisons consider the effect of leaving diluted, decanted samples before analysis. This involves comparing batch A with successively batches B, C, D & E. Minus 190 micron material from bulk sample sites B, G and Y was analysed for Cu, Pb, Zn Fe and Mn for batches A, B & C, and for Zn for batches D & E.



Batch A    diluted, decanted, analysed at once as control.  
Batch B    diluted, decanted, analysed after 24 hours.  
Batch C    diluted, decanted, analysed after 3 days.  
Batch D    diluted, decanted, analysed for Zn only after 7 days.  
Batch E    diluted, decanted, analysed for Zn only after 11 days.  
Batch F    diluted after 24 hours, decanted and analysed.  
Batch G    diluted after 72 hours, decanted and analysed.  
Batch H    diluted, decanted after 24 hours, then analysed.  
Batch J    diluted, decanted after 72 hours, then analysed.

Figure 5.1 shows, schematically, the number of significantly similar comparisons. After 24 hours, 9 of the 15 combinations are significantly similar, and after 3 days, only 3 out of 15 are still similar. Increasing the standing time to 7 and 11 days increased still further the dissimilarity. By 11 days, observation showed that the volume of sample liquid had decreased, probably due to evaporation, which may explain the observed increase in metal content. This idea was pursued further by taking another batch of samples and storing them in containers with clip-on plastic lids. These samples, left for 5 days, showed no significant difference in Cu, Pb, Zn, Fe and Mn content when compared with the control set. Two further sets of 6 samples were stored, uncovered, for 3 and 5 days, one set in 10 ml beakers, the other in 50 ml beakers. The surface area of the sample liquid in the larger beaker was approximately three times that of the liquid in the smaller beaker, and therefore a more rapid increase in metal content in samples in the larger beakers was anticipated if

	Cu	Pb	Zn	Fe	Mn
Site B	*	*	*		
Site G	*	*	*	*	
Site Y	*		*		

Comparison batch A vs. batch B.

	Cu	Pb	Zn	Fe	Mn
Site B					
Site G			*	*	
Site Y	*				

Comparison batch A vs. batch C.

	Zn
Site B	
Site G	
Site Y	

Comparison batch A vs. batch D.

	Zn
Site B	
Site G	
Site Y	

Comparison batch A vs. batch E.

An asterisk denotes difference value less than  
Fisher's Least Significant difference at  $\alpha = 0.01$ .

FIGURE 5.1. RESULTS OF ANALYSIS OF VARIANCE FOR BATCHES A,B,C,D & E

the change is due to evaporation. Table 5.4 summarises the results of this comparison.

A further attempt to investigate the effects of evaporation involved the weighing of liquid samples before and after storage. Blanks were left exposed to the air in an attempt to detect atmospheric contamination. The Zn content of 20 sample leaches was determined, and eight of them covered with airtight lids. They were weighed and stored, along with six blanks, for 4 days, before being re-weighed and re-analysed. The metal concentration in solution was determined following the first analysis and, assuming a specific gravity of 1.0 (see Section 5.2.3.7), corrections made taking due account of the observed weight losses caused by evaporation. These results are compared with those from the re-analysis in Table 5.5. It may be seen that agreement between concentrations calculated from the weight loss by evaporation are in very good agreement with those from re-analysis. The use of air-tight plastic lids prevented evaporation, and results from samples so covered were in good agreement with the original values. De-ionised water and dilute acid blanks, left for the same period, were all below detection limits when re-analysed.

It may thus be concluded that the observed increases in metal content in stored sample leaches were due to evaporation, not atmospheric contamination, and that if liquid sample leaches are to be stored for even 24 hours, such evaporation losses must be avoided by the use of air-tight lids for the storage containers.

TABLE 5.4: Comparison of samples left uncovered in 10 ml and 50 ml beakers. Figures represent average % increase for six samples.

	<u>3 days storage</u>		<u>5 days storage</u>	
	10 ml beaker	50 ml beaker	10 ml beaker	50 ml beaker
Cu	15.0	24.9		
Pb	13.1	23.6		
Zn	16.8	19.0	73.3	203
Fe	6.5	14.2		
Mn	8.9	18.1		

**TABLE 5.5:** Zinc results for samples left for four days subject to evaporation loss.

Sample number	Weight loss in 4 days (g)	Original reading	Second reading	Calculated concentration
1 C	0.00	31	32	31
2 NC	0.51	34	43	40
3 NC	0.51	62	76	73
4 C	0.01	89	85	89
5 NC	0.49	96	109	113
6 NC	0.49	151	170	177
7 C	0.01	132	128	132
8 NC	0.50	130	160	153
9 NC	0.50	128	165	150
10 C	0.00	153	145	153
11 C	0.01	120	120	120
12 NC	0.42	170	195	194
13 NC	0.42	230	260	263
14 C	0.01	315	310	316
15 NC	0.40	305	340	348
10 NC	0.41	320	375	365
17 C	0.01	365	375	366
18 NC	0.50	405	480	478
19 NC	0.46	425	495	496
20 C	0.02	435	445	438

C denotes sealed with plastic lid

NC denotes not sealed with lid.

All values of concentration in ppm Zn.

The second part of this experiment investigated the effects of storing samples in the test tubes in which they were digested, and therefore still in contact with the solid sample material.. This involved comparison of batch A with batches F, G, H and J and also comparison of batches G and J. The comparisons are shown, schematically, in Figure 5.2, and demonstrate that the samples which were diluted before storage (H & J) showed a more rapid change when compared with the control set (A) than did those which were stored undiluted (F & G), although the net result after 72 hours was very similar (G vs. J). Again, the evidence suggests that storage of samples is inadvisable, although if any chemical interaction between liquid leach and solid sample residue took place, it was unaffected by diluting the samples prior to storage.

It may, therefore, be concluded that ideally samples should be analysed as soon as possible after digestion. Where this proves impracticable, samples should be stored beneath an air-tight seal to prevent liquid loss by evaporation. For periods up to 72 hours, there appears to be little evidence of chemical interaction between liquid leach and solid residue if samples are stored in test-tubes, and indeed evaporation losses may well be minimised by this technique, since comparison A to J showed 9 out of 15 similar combinations after 72 hours, whereas comparison A to C had only 3. However, lids to seal test-tubes are not generally available, whereas the 10 ml beakers used are supplied with tight-fitting lids. It is considered desirable to decant samples before analysis because this practice removes the risk of aspirating solid sample residues into the AAS, thus blocking the nebuliser input tube.

Comparison batches A vs. F.

	Cu	Pb	Zn	Fe	Mn
Site B	*	*	*	*	
Site G	*	*	*	*	*
Site Y	*	*			

Comparison batches A vs. G

	Cu	Pb	Zn	Fe	Mn
Site B	*	*	*		
Site G	*		*		*
Site Y	*				

Comparison batches A vs. H.

	Cu	Pb	Zn	Fe	Mn
Site B	*	*	*		
Site G	*		*		*
Site Y	*				

Comparison batches A vs. J.

	Cu	Pb	Zn	Fe	Mn
Site B	*	*	*	*	
Site G	*		*		*
Site Y	*	*			

Comparison batches G vs. J.

	Cu	Pb	Zn	Fe	Mn
Site B	*	*	*	*	*
Site G		*	*	*	*
Site Y	*	*	*	*	*

An asterisk denotes difference value less than Fisher's Least Significant difference at  $\alpha=0.01$ .

FIGURE 5.2: RESULTS OF ANALYSIS OF VARIANCE FOR BATCHES A, F, G, H & J.

### 5.3.2. Readings obtained as a function of sample weight.

#### 5.3.2.1 Outline of problem.

During the experiment, described in Section 2.3 (p.2.8) to determine an optimum sample weight, a general decrease in the reported metal contents of samples was observed as the weight of sample taken was increased. As an example, data for 0.05g and 0.5g sample weights of minus 125 micron material from bulk sites B, G and Y is presented in Table 5.6. While the lower sample weight did not always result in a higher metal content reading, it was sufficiently consistent to be considered worthy of investigation. Table 5.7 demonstrates that this phenomenon occurred in other mesh fractions.

The heavy and light mineral fractions from sites B and G were also analysed in similar fashion (Section 2.3.3.3., p. 2.32) and the results confirm the same general trend.

Seven samples from Yarner Wood were selected, and portions of 0.05g and 0.5g of each digested in a 10% (w/v) ammonium citrate/hydroxylammonium chloride solution. The results for Cu, Zn and Co were approximately 30% lower for the larger weight, compared with those for the smaller sample, and for Fe, more than 50% lower, whilst for Mn, only a slight difference was observed (Table 5.8).

#### 5.3.2.2. Balances check.

The first possible cause of these differences to be examined was torsion balances. During the entire project, only two torsion balances were used to weigh samples prior to analysis, with a maximum load of 0.25g for the 0.05, 0.1 and 0.2g samples, and one with a 1.0g maximum for the remainder. Ten lots of 0.05g of Site B, minus 125 micron



material, were weighed out on each of the two balances, and the results are shown in Table 5.9.

None of the differences observed are significant at the 95% confidence level and the conclusion is therefore that the balances were not responsible for the observed discrepancy.

TABLE 5.6: Comparison of means of Cu, Pb, Zn, Fe and Mn for 0.05g and 0.5g sample weights of minus 125 micron material, bulk sample sites B, G and Y.

	<u>0.05g</u>	<u>0.5g</u>	<u>Test</u>	<u>Result</u>
Site B	mean	mean		
Cu	106	91	t	SIG
Pb	98	64	s	SIG
Zn	180	150	s	SIG
Mn	612	650	s	SIG*
Site G				
Cu	704	630	t	SIG
Pb	9910	9290	t	SIG
Zn	590	543	s	SIG
Fe	50900	46750	t	SIG
Mn	852	752	s	SIG
Site Y				
Cu	30	31	s	NS
Pb	79	78	s	NS
Zn	111	103	t	SIG
Fe	14450	14290	t	NS
Mn	514	488	t	SIG

For the sake of brevity in this and subsequent tables which show comparisons of means, only the means are quoted, along with the type of test applied, t denoting Student's t test, and s denoting Standard Error of difference test, and the result of the comparison.

n = 10 throughout

SIG denotes difference significant at  $\alpha = 0.05$

NS denotes difference not significant at  $\alpha = 0.05$

\* denotes 0.5g mean greater than 0.05g mean.

All values in ppm.

**TABLE 5.7: Means for various sample weights and various mesh fractions, Site B.**

<u>Cu</u>	0.05g	0.1g	0.2g	0.3g	0.5g	1.0g
Mesh size (microns)						
-660	42	48	47	47	47	45
-660+190	45	40	37	37	35	37
-190	75	75	74	76	75	75
-190+140	61	60	58	58	57	56
-140	92	97	88	90	85	82
-140+125	77	72	72	67	68	64
-125	106	95	94	93	91	89
-125+70	93	91	88	83	83	81
-70	102	102	99	100	99	95
 <u>Zn</u>						
-660	88	89	85	82	81	80
-600+190	75	71	71	69	65	61
-190	153	142	135	138	131	129
-190+140	109	104	97	96	96	97
-140	166	156	146	144	140	139
-140+125	145	132	123	123	113	116
-125	180	167	165	156	150	150
-125+70	165	153	149	146	142	142
-70	184	182	173	171	167	168

all values in ppm.

each is mean of 10 analyses.

**TABLE 5.8:** Results for 0.05g and 0.5g portions of selected samples from Yarnar Wood, digested in 10% (w/v) solution of ammonium citrate and hydroxylammonium chloride.

Sample number	<u>Cu</u>		<u>Zn</u>		<u>Co</u>		<u>Mn</u>		<u>Fe</u>	
	0.05g	0.5g	0.05g	0.5g	0.05g	0.5g	0.05g	0.5g	0.05g	0.5g
YW 9A	36	24	20	16	10	6	200	180	800	400
YW 10A	366	276	68	50	105	86	2420	2080	2600	1080
YW 12A	190	142	76	59	60	51	1340	1320	1500	700
YW 23A	200	158	182	164	60	51	3240	3300	2200	970
YW 33A	46	27	454	300	60	43	ND	ND	2500	1380
YW 47A	8	5	24	10	15	4	100	80	1200	540
YW 60A	46	25	ND	ND	30	29	ND	ND	6100	2450
Mean	127	94	137*	100*	49	39	1460**	1392**	2414	1074

ND denotes not determined

\* denotes mean of 6 values

\*\* denotes mean of 5 values

All values in ppm determined by AAS

**TABLE 5.9:** Comparison of results for 0.05g weights of site B, minus 125 micron material, using different balances

Element	Mean value 0.25g balance	Mean value 1.0g balance	Test	Result
Cu	100	101	t	NS
Pb	57	52	t	NS
Zn	186	189	s	NS
Fe	26,080	26,380	t	NS
Mn	640	644	t	NS

Legend as for Table 5.6

#### 5.3.2.3. Settling temperature.

Digested samples are diluted to some fixed volume, shaken and allowed to settle, prior to decanting ready for analysis. It was suggested that the discrepancy under examination might be brought about by some chemical re-sorption of metal from the solution onto the solid phase, during this period of settling. The temperature at which settling takes place may be critical, metal remaining in solution at higher temperature, but the equilibrium being displaced in favour of the solid phase by a lowering of temperature. In an attempt to investigate this possibility, two batches of samples were digested simultaneously. After dilution and shaking, one batch was allowed to settle at room temperature, whilst the other was put

back into the hot water bath. The results, summarised in Table 5.10 indicate that the discrepancy was present to a similar extent whether the samples were allowed to settle at room temperature or at 95°C, and that temperature dependent chemical re-sorption is therefore not its cause.

TABLE 5.10

Element	Settling	Mean 0.05g	Mean 0.5g	Test	Result
Cu	Hot	109	96	s	SIG
Cu	Cold	112	98	t	SIG
Pb	Hot	67	65	s	NS
Pb	Cold	68	65	t	NS
Zn	Hot	187	162	s	SIG
Zn	Cold	185	166	s	SIG
Fe	Hot	26,800	24,340	t	SIG
Fe	Cold	27,350	25,680	t	SIG
Mn	Hot	694	672	s	SIG
Mn	Cold	674	649	t	NS

Legend as for Table 5.6

#### 5.3.2.4. Alternative analytical configurations.

Two alternative configurations on the AA Spectrophotometer itself were adopted in attempts to eliminate the discrepancy in sample concentration. Analysis for Cu was conducted with the burner head rotated through 30°, thus substantially reducing the light path in the flame. Analysis was also carried out at the less sensitive resonance line of 327.4 nm, rather than the usual 324.7 nm.

With the rotated flame, the mean concentration of the 0.05g samples was 95.0 ppm and of the 0.5g samples was 84.2 ppm. Both sets were diluted to 10 ml final volume. A comparison of these two means by the Standard Error of Difference test shows this difference to be significant at 95% confidence level.

The mean Cu contents of 0.05g and 0.5g samples analysed on the 327.4 nm resonance line were 106.0 ppm and 93.0 ppm respectively. In this case a Student's t test is appropriate, and again the difference in means is significant, even at the 99% confidence level.

Thus, two alterations in instrument configuration, commonly applied to increase linear response when dealing with concentrated samples, were shown to have no effect on this particular problem.

#### 5.3.2.5. Rigour of attack

It was suspected that an increased weight of sample might reduce the efficiency of the acid attack, possibly by neutralising the acid, or by reducing acid circulation through the larger sample mass in the bottom of the test tube.

In consequence, various volumes of acid were tried both in test tubes and in 50 ml beakers. 0.05 and 0.5g samples were subjected to digestion in 5, 10, 15 and 20 ml of 4M  $\text{HNO}_3$  at 95°C for 4 hours in test tubes and also in 20 and 40 ml of acid in beakers.

Tables 5.11 and 5.12 show that, with the exception of Mn, the reported concentration for the 0.05g sample weight was consistently higher than that for 0.5g regardless of the volume of acid used or the shape of the container in which the digestion was carried out. It may, therefore, be assumed that the cause of the discrepancy in metal

values is not neutralisation of acid during digestion, nor restriction in circulation of acid in the bottom of test tubes during the digestion of large sample weights.

The circulation of acid in the bottom of test tubes was further investigated by analysing 0.5g of site G, minus 190 micron material for Pb, and comparing the result with that obtained from the analysis of 0.05g of the same material which was digested mixed with 0.45g of "spec. pure" silicon dioxide. Pb was the element chosen because Table 5.6 shows that it demonstrates the effect particularly well. The 0.05g sample (with the  $\text{SiO}_2$ ) reported 6400 ppm Pb, whilst the 0.5g sample reported only 5800 ppm. It seems, therefore that acid circulation was not impaired by the addition of 0.45g of non-Pb bearing material to the smaller sample.

The pH of leaches derived from the digestion of 0.05 and 1.0g samples was measured directly. The samples were digested in 5ml of 4M  $\text{HNO}_3$  for 4 hours at 95°C, then diluted to 10 ml with the de-ionised water, prior to measurement on a pH meter.

Table 5.13 shows that digesting a larger sample did significantly increase the pH of the leach, but the mean value after digestion of 1.0g was only 0.185, which still represents very strong acid, compared with 0.085 for the 0.05g sample.

#### 5.3.2.6. Extent of dilution.

Digestion of 0.05g and 0.5g portions of minus 125 micron material from site G, was carried out. Because absolute metal values are much higher at site G than at site B, it was necessary to dilute the 0.5g samples to 100 ml instead of the usual 10 ml, so that they could be conveniently read on the AAS. The differences in means

**TABLE 5.11** Comparison of means for various volumes of acid used in digestion. Material, Site B, minus 125 micron.

Digestion	Element	0.05g mean	0.5g mean	Test	Result
5ml TT	Cu	106	91	t	SIG
	Pb	98	64	s	SIG
	Zn	180	150	s	SIG
	Mn	612	650	s	SIG*
10ml TT	Cu	112	93	t	SIG
	Pb	90	68	s	SIG
	Zn	200	168	t	SIG
	Fe	26,250	22,890	t	SIG
	Mn	668	670	t	NS
15ml TT	Cu	115	9	t	SIG
	Pb	98	66	s	SIG
	Zn	202	168	t	SIG
	Mn	601	621	t	SIG*
20ml TT	Cu	108	90	s	SIG
	Pb	99	62	s	SIG
	Zn	195	160	t	SIG
	Mn	580	595	s	NS
20ml BK	Cu	114	88	s	SIG
	Pb	94	61	s	SIG
	Zn	190	155	s	SIG
	Mn	586	601	t	SIG*
40ml BK	Cu	101	79	t	SIG
	Pb	103	57	s	SIG
	Zn	173	145	t	SIG
	Mn	507	540	s	SIG*

TT denotes digestion in test tubes.

BK denotes digestion in beakers.

Remainder of Legend as for Table 5.6.



TABLE 5.12 Comparison of results obtained from 20 ml digestion in test tubes and in beakers. Material Site B, minus 125 micron.

Sample Weight	Element	TT mean	BK mean	Test	Result
0.05g	Cu	108	114	s	NS
	Pb	99	94	t	NS
	Zn	195	190	t	NS
	Mn	580	586	t	NS
0.5g	Cu	90	88	t	NS
	Pb	62	61	t	NS
	Zn	160	155	t	SIG
	Mn	595	601	t	NS

Legend as for Table 5.11

at the 95% confidence level, shown compared in Table 5.14, are only significant for one of the five elements, Zn. It therefore seems likely that the overall strength of the solution analysed may be the crucial factor in controlling how much metal is reported via the AAS.

This fact may also help to explain some observed peculiarities in the original data from Section 2.3. For example, in Table 5.6, the results for Site Y show that differences for Cu, Pb and Fe are not significant. However, the 0.5g samples, upon which these comparisons are based, had been diluted to 20ml, whereas the 0.05g samples were diluted to 10ml, and this change in dilution may be in part responsible for the agreement being better than anticipated.

TABLE 5.13 Measurements of pH on sample leaches following digestion.

Sample No.	pH (0.05g)	pH (1.0g)
1	0.15	0.20
2	0.10	0.15
3	0.05	0.20
4	0.10	0.20
5	0.05	0.10
6	0.05	0.20
7	0.10	0.15
8	0.05	0.25
9	0.10	0.20
10	0.10	0.20
Mean	0.085	0.185
Variance	$1.139 \times 10^{-3}$	$1.694 \times 10^{-3}$
F	= 1.49	
$F_{(0.025,9,9)}$	= 4.03	
Sp = Pooled Estimate of Standard Deviation = $3.764 \times 10^{-2}$ .		
t	= 5.94	
$t_{(0.925,18)}$	= 2.10	

Therefore Observed difference is significant at  $\alpha = 0.05$ .

Sample material, Site G, minus 125 micron.

**TABLE 5.14** Comparison of means for 0.05g and 0.5g samples of material from Site G, minus 125 micron, diluted to different final volumes.

Element	Mean 0.05g	Mean 0.5g	Test	Result
	DT 10 DIW	DT 100 DIW		
Cu	652	666	t	NS
Pb	9680	9860	s	NS
Zn	547	608	t	SIG*
Fe	48300	48800	t	NS
Mn	850	868	t	NS

DT (10/100) DIW denotes diluted to 10 or 100 ml with de-ionised water.

Remainder of Legend as for Table 5.6

#### 5.3.2.7. Interferences.

The occurrence of interference during analysis by AAS is well-known, and documented in most texts on the subject. The fact that the presently observed discrepancy cannot be explained in terms of the aspects of technique so far described in this Section, but that it does appear to be sensitive to the concentration of the sample, i.e. the degree of dilution, implies that it probably falls within the realm of interferences. Welz (1976) defines interference as a difference in behaviour between samples and reference substances, leading to an invalidation of the comparisons which make AAS a

quantitative method. Depending on their origin, the majority of interferences may be classified as chemical, physical, background or spectral.

Spectral interferences are rare in AAS work, especially if single-element lamps are employed and would not be expected to influence so wide a range of elements as those examined in the present study. In addition, dilution of samples would be unlikely to have any proportionate effect upon such interference.

Background interference is caused by light scattering on solid or liquid particles in the flame, and by absorption of light by molecules from the sample matrix. The use of a deuterium arc background corrector is generally recommended for the removal of background interference effects. Samples of 0.05g and 0.5g weights of the heavy mineral fraction of Site G, minus 70 micron material, were digested. The 0.05g and 0.5g samples were diluted to 10ml and the 0.5g also to 100 ml. They were then analysed with the deuterium corrector in operation and the results are summarised in Table 5.15.

From this Table it can be seen that the discrepancy is still present for each comparison involving an 0.5g sample diluted to 10ml, but that dilution to 100 ml renders any difference insignificant. Therefore, the interference under examination is not contributed to significantly by background effects.

Physical interferences are brought about by differences in the physical properties of samples, notably specific gravity, surface tension, and viscosity. Such changes result in samples being aspirated at differing rates, and thus different amounts of sample reach the flame. The specific gravities of five 0.05g leaches, and five 0.5g

**TABLE 5.15** Comparison of results for 0.05g and 0.5g samples diluted to 10ml and 100ml using deuterium background corrector

Element	Mean 0.05g	Mean 0.5g DT 10	Mean 0.5g DT 100	Test	Result
Cu	760	694		t	SIG
	760		727	s	NS
Pb	6,680	4,860		t	SIG
	6,680		6,500	t	NS
Zn	639	554		t	SIG
	639		665	s	NS
Fe	49,000	44,960		t	SIG
	49,000		48,500	t	NS

DT 10 denotes diluted to 10 ml

DT 100 denotes diluted to 100 ml.

Remainder of Legend as for Table 5.6.

leaches, all diluted to 10 ml, were measured. The mean SG of the 0.05g leaches was 1.0648 and that of the 0.5g leaches was 1.0645. A Student's t test to compare the difference in means found it to be not significant, even at the 90% confidence level. The time taken for the aspiration of successive 0.5ml aliquots of leaches from 0.05g and 0.5g samples, diluted to 10 ml, has been measured as a means of examining for possible differences in viscosity. The mean times for aspirating 0.5 ml aliquots were 6.85 seconds for 0.05g samples, and 7.16 seconds for 0.5g samples. A Student's t test shows the difference in means is not

significant even at the 90% confidence level. However, the difference in aspiration times observed is of the right order of magnitude to account for most of the observed discrepancies, even though the method of timing employed was somewhat crude. Further work might be usefully concentrated on devising a better controlled experiment to see how real is the difference in aspiration time. On the present evidence, though, an alternative to physical interference should be sought.

Chemical interference causes a reduction in the number of free atoms in the flame brought about by the formation of chemical compounds involving the cations under consideration. A low level of achievable sensitivity will be experienced for elements which readily form stable compounds with the combustion products of the flame, thus preventing their forming free atoms. However, this form of interference is independent of sample matrix, and is not of concern in the present investigation.

The quantitative dissociation of molecules into free atoms in a flame is a temperature dependent, equilibrium reaction. In a dynamic medium like a flame, it is also time dependent, and one possible source of chemical interference is that the sample material passes through the flame too quickly, and has risen beyond the light beam before atomisation has reached equilibrium. This possibility may be investigated by measuring in a higher part of the flame. In order to see whether such a process has any bearing on the present investigation, measurement was made of the Cu content of batches of 10 0.05g and 0.5g samples of Site B, minus 140 micron material, all diluted to 10 ml, with the centre of the light beam passing 5 mm higher in the flame than in normal operation. The mean copper content of the 0.05g samples was

97.4 ppm, and that of the 0.5g samples 87.3 ppm. When subjected to a Student's t test, the difference proved to be significant even at the 99% confidence level. The respective mean concentrations for determination at the normal burner position were 99.4 and 90.2 ppm. indicating that equilibrium dissociation has taken place with the burner head at its normal position, and that this is not the source of the observed interference.

An alternative method of pushing the dissociation equilibrium between molecules and free atoms further to the right is to use a hotter flame. Whilst the manufacturers' handbook (Perkin Elmer, 1973) recommends an air/acetylene flame for all the elements presently under consideration, a nitrous oxide/acetylene flame was tried as an alternative because of its high temperature (2750°C approx.) and its strongly reducing nature. The same samples, as referred to in the previous paragraph, were analysed using the nitrous oxide/acetylene flame and the mean Cu concentrations were, for 0.05g samples, 131 ppm, and for 0.5g samples, 101 ppm. A standard error of difference test showed the difference to be significant even at the 99% confidence level.

Having failed to remove the observed interference by altering the method of atomisation, an attempt was made to remove it chemically. It has already been noted that matching matrix concentration by extra dilution of large weight samples improves the situation (see Table 5.14), and attempts were made to determine the effects of altering the chemistry of the diluting solutions. Lanthanum chloride is commonly added when AAS determinations are being carried out in an air/acetylene flame, as the lanthanum preferentially combines with a number of potentially interfering anions during the evaporation stage. Four different strengths of AAS purity lanthanum chloride solution were used to dilute batches of 3 samples of 0.05g and 0.5g weight of Site B, minus 125 micron material, making 24 samples in all. Because there are

only three samples in each batch, it is felt that mean and variance calculations are inappropriate. Therefore, in Table 5.16, the value quoted is the mean of the 3 values for 0.5g expressed as a percentage of the mean of the 3 values for 0.05g.

TABLE 5.16 Comparison of 0.05g and 0.5g samples diluted to 10ml with various strengths of  $\text{LaCl}_3$  solution.

Element	0.1% Soln.	0.5% Soln.	1.0% Soln.	2.0% Soln.
Cu	107	111	96	95
Pb	85	93	105	82
Zn	89	94	92	92
Fe	87	94	91	82
Mn	101	99	97	91

Each figure represents the mean concentration for the 3 x 0.5g samples expressed as a % of the mean of the 3 x 0.5g samples.

The pattern, displayed by Table 5.16, is somewhat confused, but the Zn and Fe results show that the closest approach to 100% comes with 0.5%  $\text{LaCl}_3$  solution. Increasing the strength beyond 0.5% causes suppression of the Cu and Mn, and to a lesser extent, Pb. As high purity lanthanum chloride solution is expensive (£16.50 per litre of 10% solution), it is desirable not to use more than necessary. Therefore, 0.5% solution was adopted as routine for further work. The experiment outlined in Table 5.14 was repeated using 0.5% lanthanum chloride solution instead of de-ionised water for dilution and the one remaining difference in means, for Zn, was reduced to a non-significant level. However, dilution of an 0.5g sample to 10ml with 0.5%  $\text{LaCl}_3$  solution only removes a small amount of the total interference effect under investigation, and whilst its routine use is considered to be good practice, it does not solve the problem in hand.



Welz (op.cit. p.101) recommends the use of EDTA as a "protective shell" to bind the cation under study so that it cannot combine with potentially interfering anions. This approach, though attractive, has not been applied because strong acid solutions destroy the EDTA, and the use of weaker sample attacks has already been rejected (see Section 2.2, p.2.3).

#### 5.3.2.8. Standards.

Reproducibility of standard solutions was investigated, as a means of determining whether the elements under consideration, Cu, Pb, Zn, Fe and Mn, are themselves responsible for the observed interference. Artificial sets of samples were created by spiking with concentrated stock solutions. The ranges of concentration were as shown below, and the analytical results are shown in Figures 5.3 to 5.12.

CS 1-10	Cu	1µg/ml	-	10 µg/ml
	Pb	10µg/ml	-	100 µg/ml
	Zn	0.5µg/ml	-	5 µg/ml
	Fe	20µg/ml	-	200 µg/ml
	Mn	0.5µg/ml	-	5 µg/ml
CS 11-20	Cu	10µg/ml	-	100 µg/ml
	Pb	100µg/ml	-	1000 µg/ml
	Zn	5µg/ml	-	50 µg/ml
	Fe	200µg/ml	-	2000 µg/ml
	Mn	5µg/ml	-	50 µg/ml

In each case the combined standards were analysed against single element standards made up in the normal way. Electronic curvature correction, for straightening non-linear responses in AAS, was used above the following levels:- Cu 2µg/ml, Pb 10µg/ml, Zn 2µg/ml, Fe 100µg/ml and Mn 20µg/ml.

Govett and Whitehead (1973) report that both suppression and enhancement of trace element concentration occurs as a result of interference largely attributed to major elements in solution, but the

trace element concentrations with which they dealt were very low, all below 10 ppm. They also noted that Cu was not subject to interference, which is not the case for the present study.

Figures 5.3 to 5.7 show that the series CS 1-10 exhibited good correlation between amount of metal present and amount detected, with the exception that a systematic under-estimation took place for Fe above 140  $\mu\text{g/ml}$ . However, the more concentrated series, Cs 11-20, shown in Figures 5.8 to 5.12, exhibited, for Cu, Pb, Zn and Fe, a consistent under-estimation resulting in the detected levels being as much as 27% short of the known content for Zn and Fe at the 50 and 2000  $\mu\text{g/ml}$  levels respectively. Mn, Figure 12, shows a close correlation between known and detected amounts of metal, with a slight positive bias in favour of detected content at 50  $\mu\text{g/ml}$ .

The exact nature of the interference giving rise to this phenomenon is something of a mystery, since the combined standards contain only de-ionised water, nitric acid and small quantities of the concentrated stock solutions used to spike them. It seems that if solutions with concentration much in excess of the levels of the CS 1-10 series are to be analysed, then a systematic under-estimation for Cu, Pb, Zn and Fe is to be anticipated, and indeed it is just such a problem which has been the subject of investigation in this section.

#### 5.3.2.9. Conclusions.

Systematic discrepancies in concentration, as a function of sample weight, have been observed during the repeated analysis of different weights of the same samples. This feature is by no means restricted in its occurrence as it was observed in mesh fractions ranging from minus 660 to minus 70 microns, from different rivers in

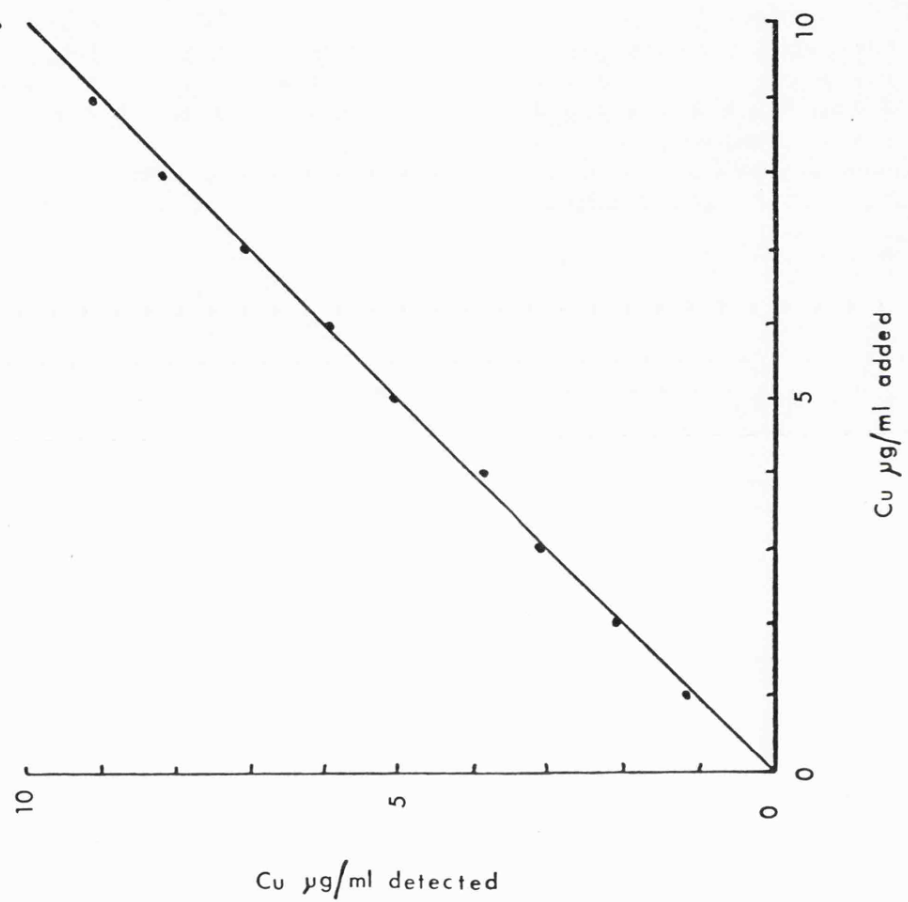


Fig. 5.3

Combined Standards C.S. 1 - 10 for Cu

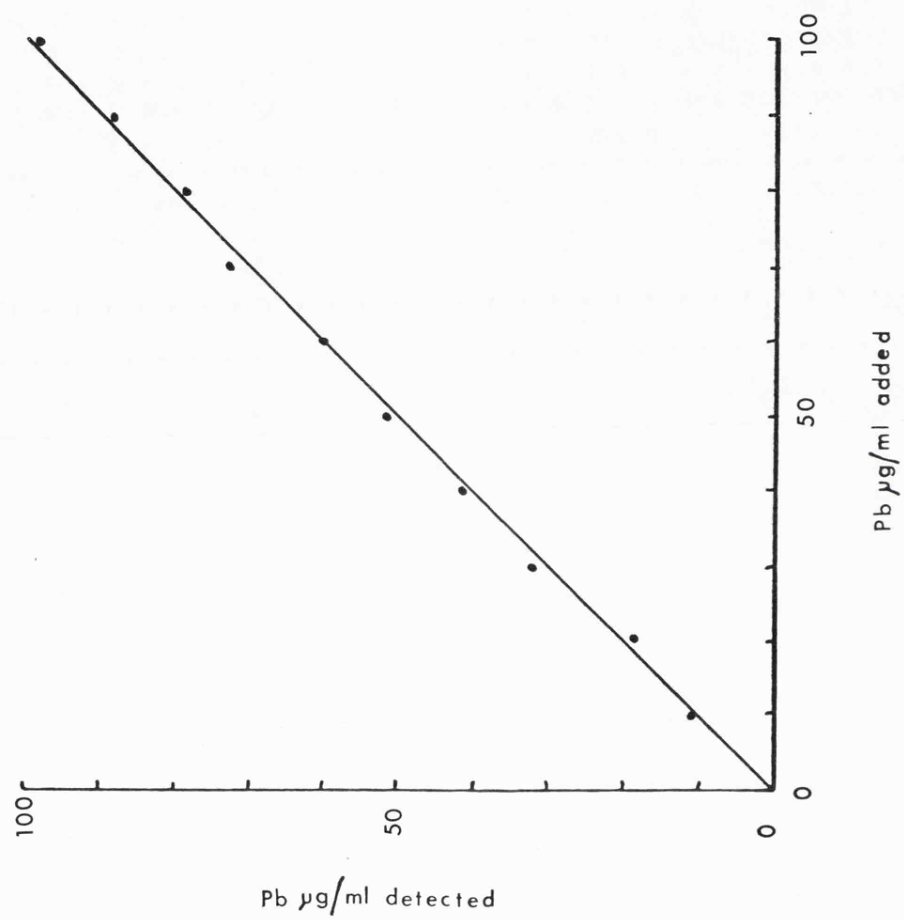


Fig. 5.4

Combined Standards C.S. 1 - 10 for Pb

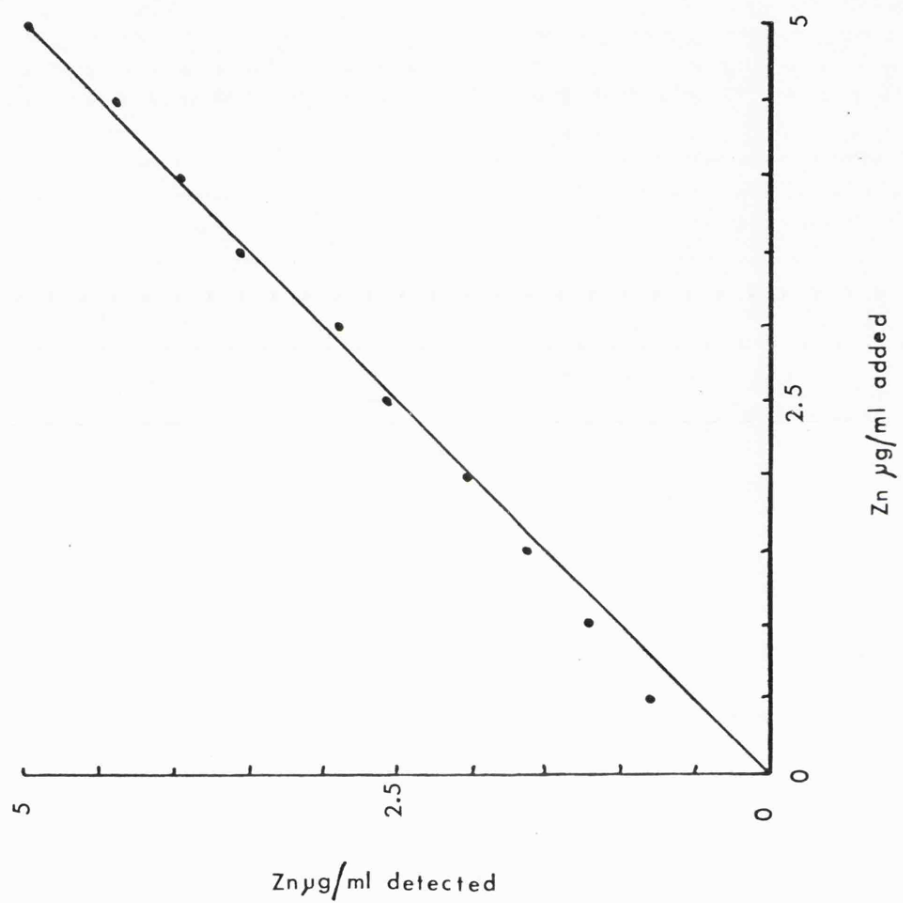


Fig. 5.5      Combined Standards C.S. 1 - 10 for Zn

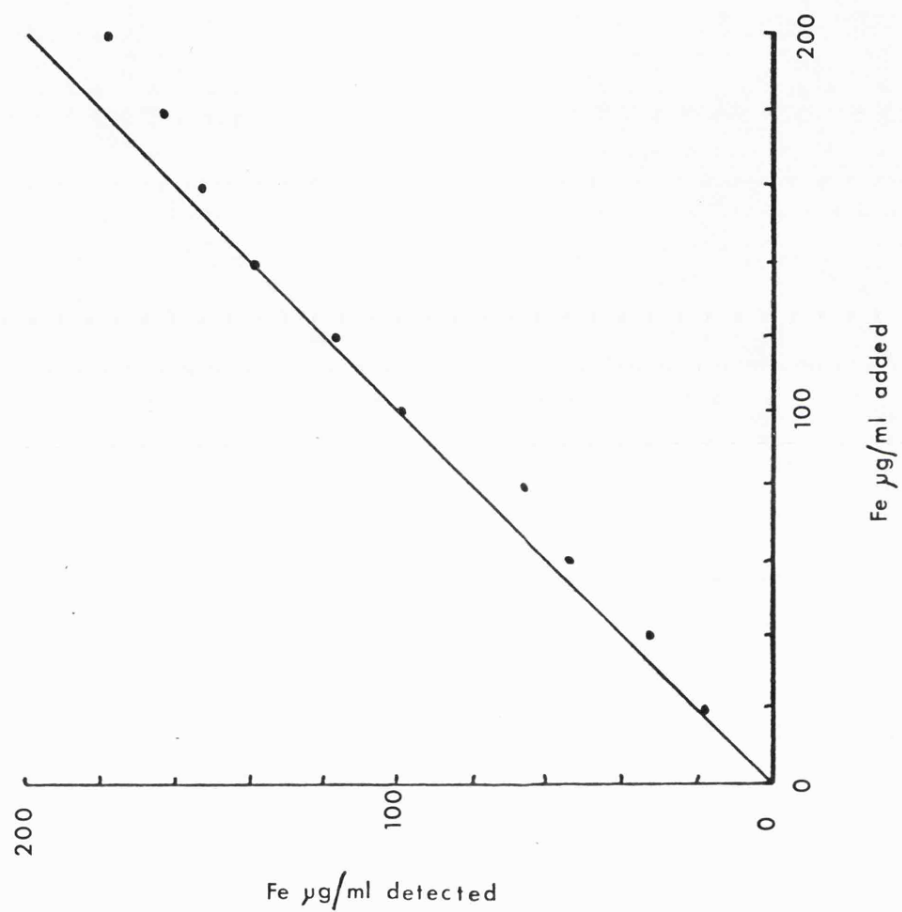


Fig. 5. 6

Combined Standards C.S. 1 - 10 for Fe

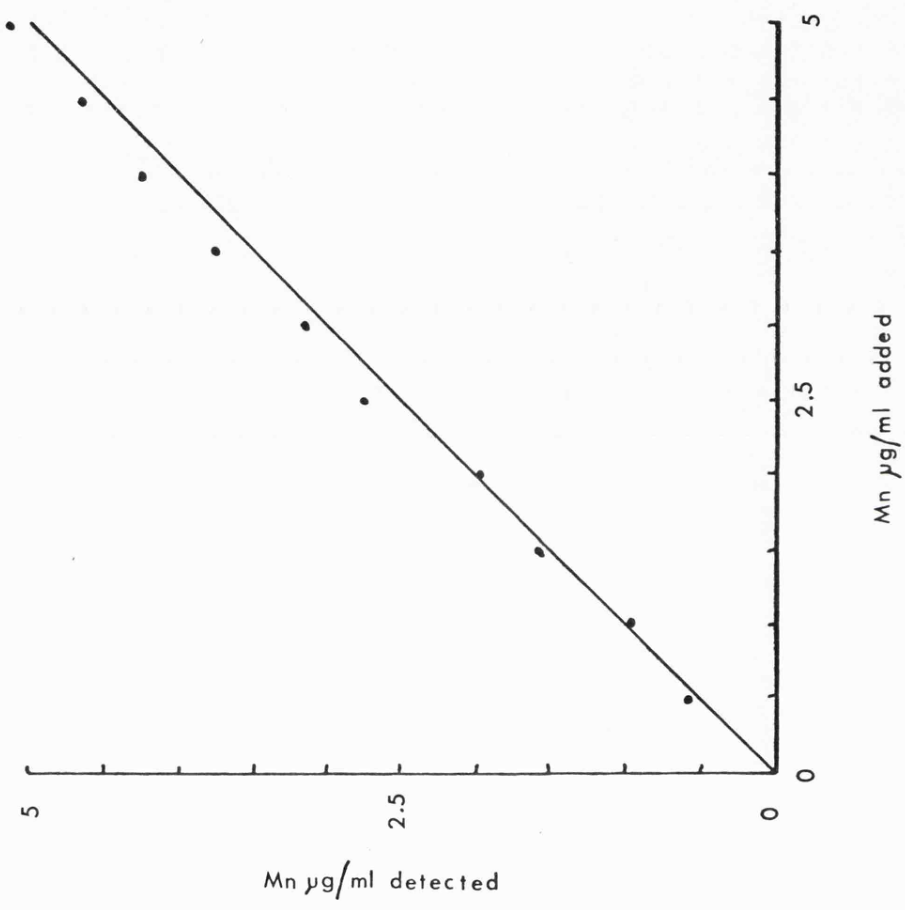


Fig. 5. 7      Combined Standards C.S. 1 - 10    for Mn

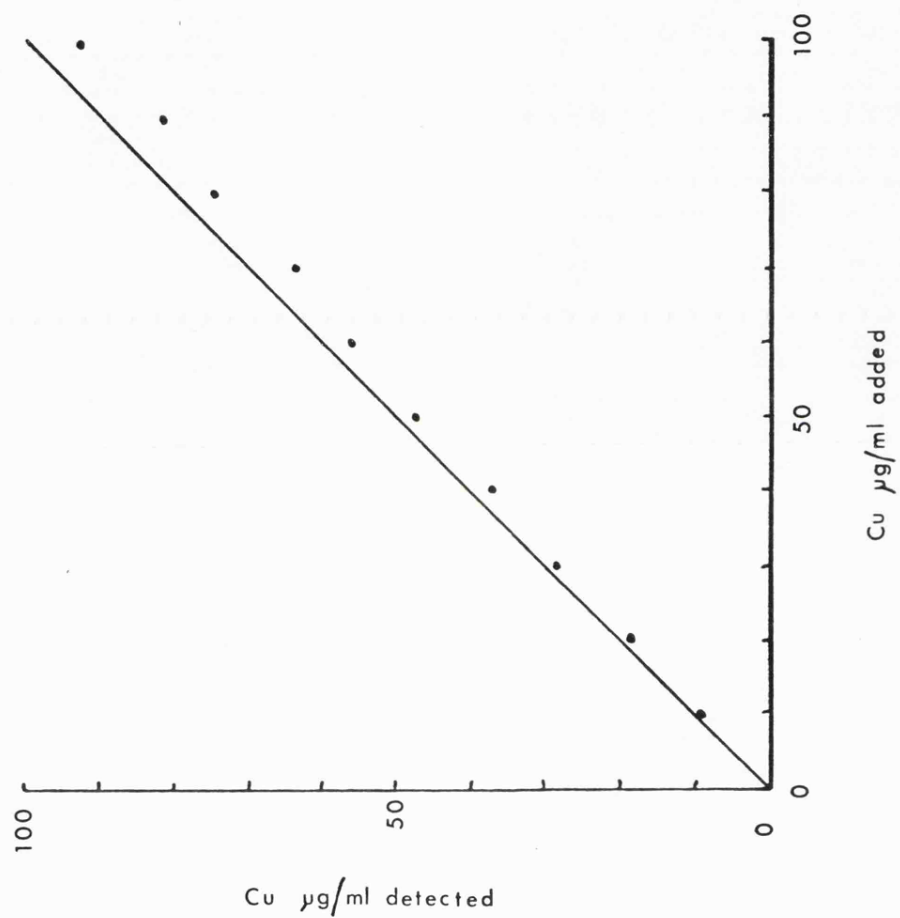


Fig. 5. 8

Combined Standards C.S. 11 - 20 for Cu



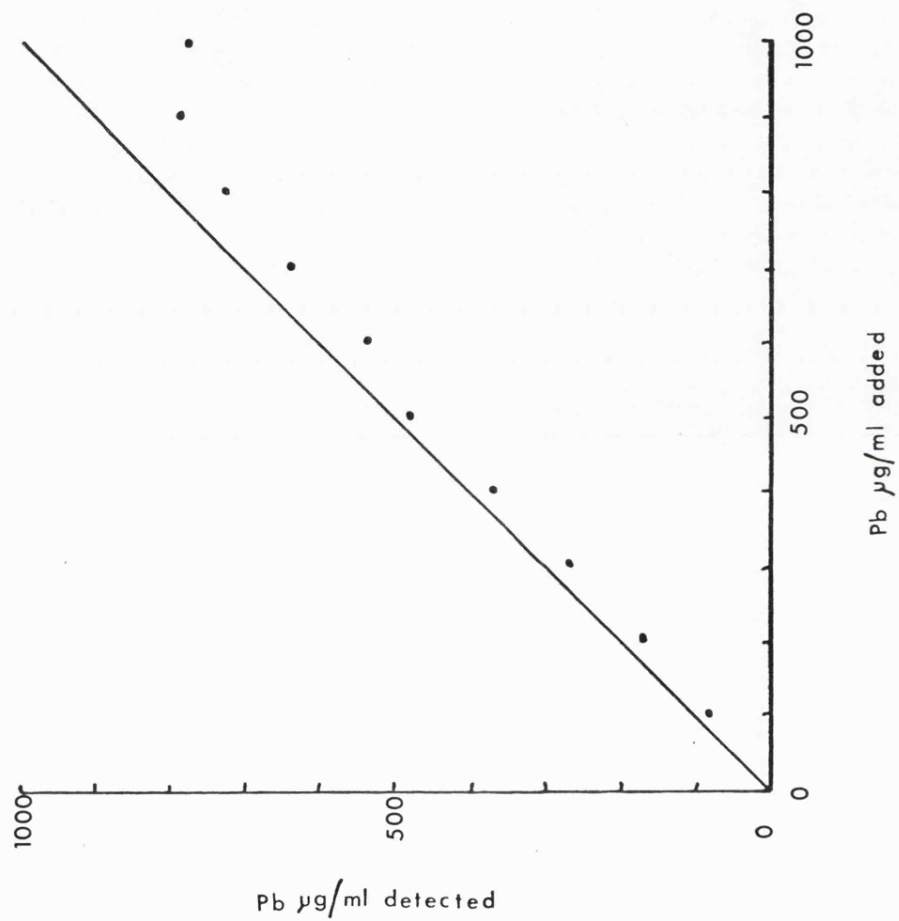


Fig. 5.9

Combined Standards C.S. 11 - 20 for Pb

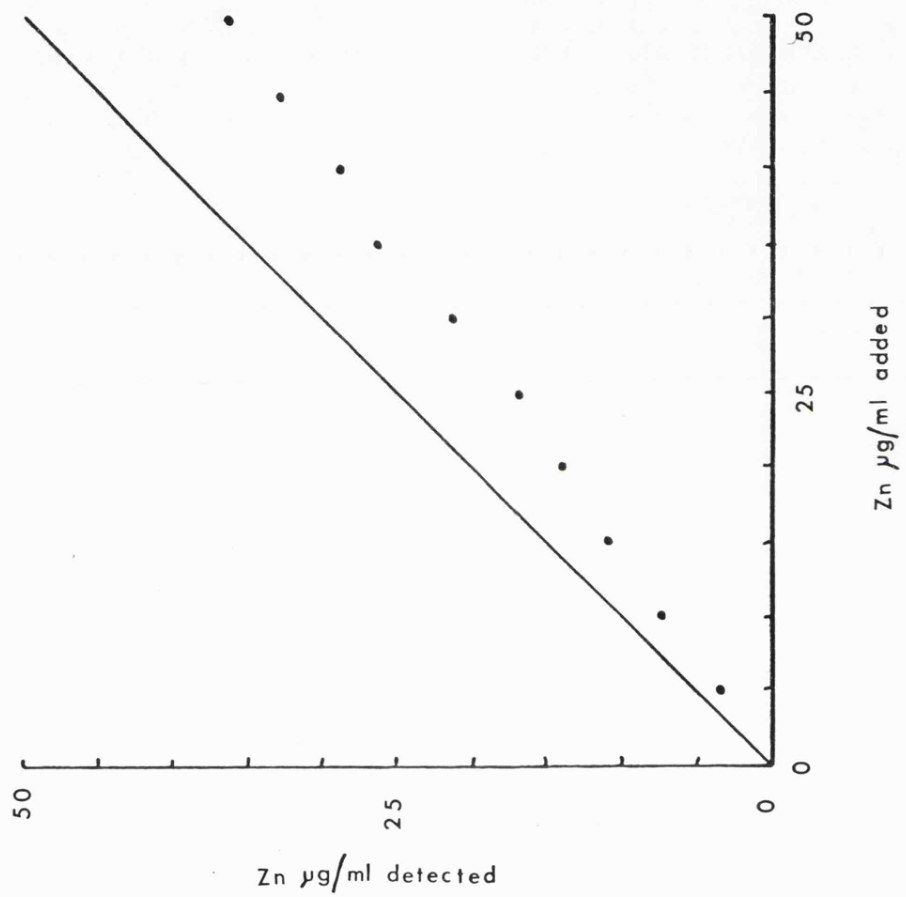


Fig. 5.10

Combined Standards C.S. 11 - 20 for Zn

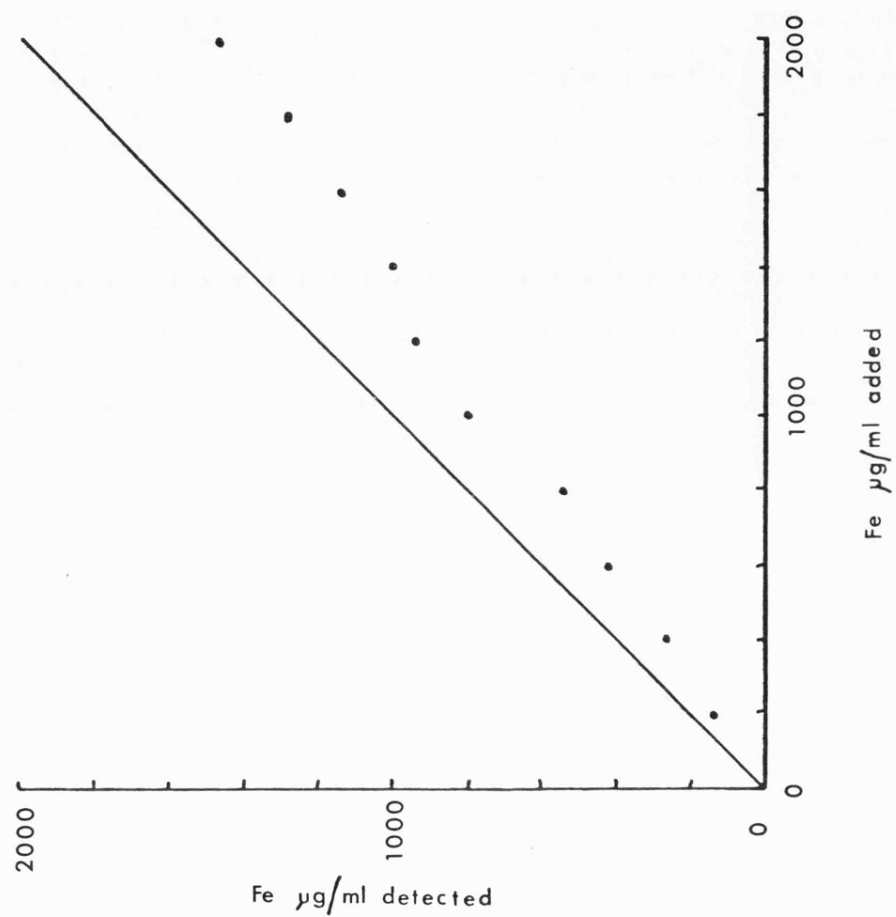


Fig. 5.11

Combined Standards C.S. 11 - 20 for Fe

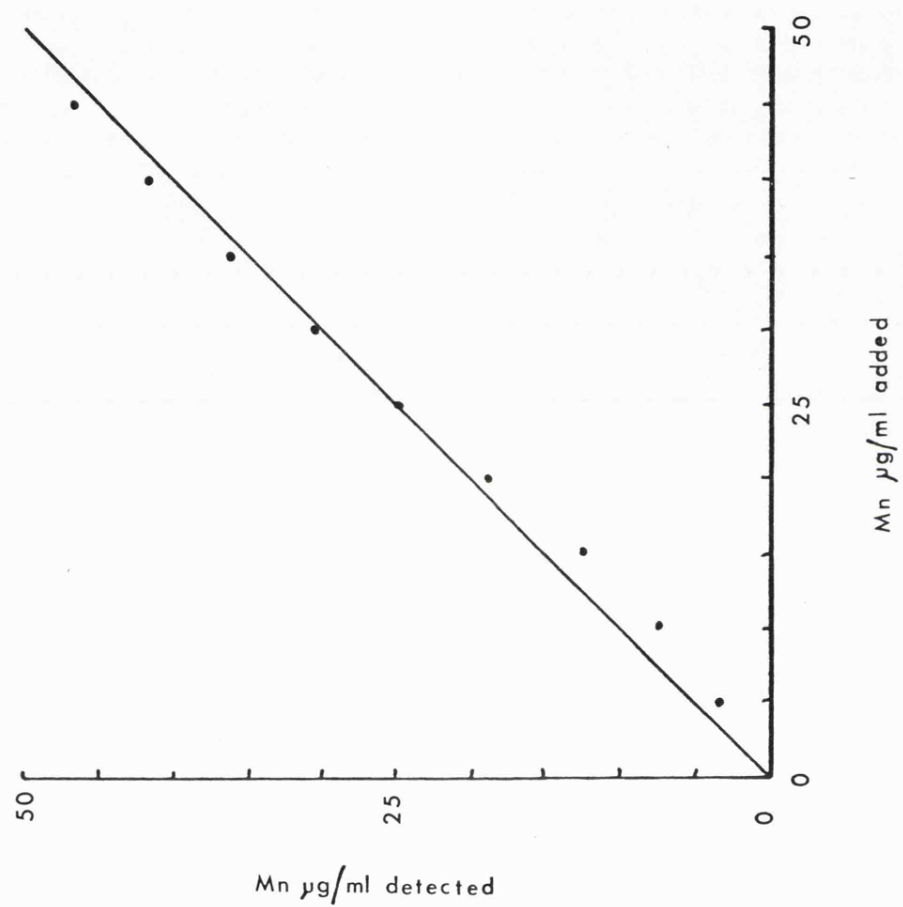


Fig. 5.12

Combined Standards C.S. 11 - 20 for Mn

areas of different headwater lithology, in heavy and light mineral fractions, and in total and cold extraction leaches.

A number of simple procedural changes were investigated and found to have no effect. For example, the balances used did not cause a systematic bias, nor did the temperature at which the samples were allowed to settle after dilution and mixing. Use of a rotated burner head and of a less sensitive resonance line during AAS analysis, methods commonly employed for overcoming non-linearity in AAS response, made no significant difference.

Increases in sample weight will obviously tend to neutralise the acid used during digestion. Also, a large amount of sample in the bottom of a test tube might inhibit circulation of acid through the sample grains. Both possibilities were investigated by using 5, 10, 15 and 20 ml acid attacks in test tubes, and 20 to 40 ml attacks in 50 ml beakers. Results of 20 ml leaches for a given sample weight were the same whether carried out in test tubes or in beakers, and the discrepancy in concentration for different sample weights remained unaffected by the volume of acid used. Direct measurement of pH on sample leaches was carried out. The results show that the pH of leaches from the larger sample were slightly and significantly higher than for smaller samples, but the final mean pH, at 0.185, still represents very strong acid.

During investigation of acid strengths, it was observed that when 0.5g samples were diluted to 100 ml and 0.05g only to 10 ml, the discrepancy in results largely disappeared. This implies that comparable analytical responses can only be achieved when matrix concentrations are similar, and further implies that interference with atomisation may be the root cause of the problem. Spectral interferences are uncommon in AAS and would not consistently affect so wide a range of elements. Background interference, caused by light scatter in the flame and/or

molecular absorption can be eliminated by using a deuterium arc background corrector. Its use made no significant difference in this case.

Differences in the physical properties of solutions cause different rates of nebulization, however the specific gravities of 0.05g and 0.5g sample leaches, both diluted to 10ml were found to be not significantly different, nor was there any significant difference in the time taken to aspirate a given volume of different samples.

Chemical interferences were considered, and the quantitative dissociation of molecules into free atoms was demonstrated by measuring in a higher region of the flame, and also by replacing the air/acetylene flame with the much hotter, reducing nitrous oxide/acetylene flame. Neither procedure caused any significant lessening of the discrepancy.

Some marginal improvement in the situation was observed after diluting samples with 0.5% lanthanum chloride solution, rather than de-ionised water, because lanthanum combines preferentially, during sample evaporation, with some potentially interfering anions in the sample matrix. This procedure, a good standard practice to adopt, adds some 0.7 pence at current prices to the cost of each digestion. The use of EDTA to bind the cations under study and carry them into the flame, free from interference, was not tried because the strong acid digestions used would destroy any EDTA added.

Synthetic samples, made with de-ionised water and nitric acid, and spiked with the metals under consideration, were analysed, and it seems that beyond certain concentrations their response on AAS, relative to single element standards, is not linear. There appears to be some overall correspondence between the elements which show this, and the levels at which it occurs, with the effects seen in the samples of

different weights. It is hoped that the present, very incomplete study of this problem may provide the basis for further work.

It may be argued that this problem is of little more than academic interest, since in a practical, routine situation the weight of sample taken will remain constant. This is so, but two situations spring immediately to mind where this behaviour may cause serious problems.

Firstly, when a sample is beyond the concentration range for which the instrument is set, either a more concentrated standard is used, on a lower amplification, or the sample is diluted until it becomes readable on the scale, or both. To dilute an anomalous sample is often the more desirable alternative, because a sample, anomalous for one element, will often be so for others too, but the present investigation has shown that dilution causes a disproportionate increase in AAS response. Section 5.3.2.8. has shown that increasing the concentration range of the standard solution does not necessarily allow the sample, even a synthetic one of known concentration, to be reliably determined. No obvious way around the problem of the anomalous sample presents itself at present, since even to re-digest the sample using a smaller sample weight, only has the same net effect as diluting the original.

The second problem is the obvious difficulty of comparing work done by different people or companies, especially when details of analytical procedure are sparse or even non-existent, as is not unknown in both company reports and even scientific papers. Thus, the geochemist trying to interpret someone else's data will be uncertain how much reliability to place on the absolute level of concentration quoted for any anomalous samples which are frequently the samples of most interest.

### 5.3.3. Determination of As

#### 5.3.3.1. Introduction.

Arsenic, in the form of arsenopyrite, is well-known in mineral deposits of S.W. England (Dines, 1956) and its presence in the secondary environment should therefore be anticipated. Acquisition of an electrode-less, UV discharge lamp for As determination prompted a trial of its use on 4M  $\text{HNO}_3$  sample leaches. The results obtained were encouraging, showing that the Yarner Wood collection of samples, 152 in all, including duplicates and Fe oxide/hydroxide rich samples, have a mean As value of 3000 ppm, ranging from 20 ppm in the River Bovey, to 23,500 ppm (2.35%) in an Fe-rich, right bank seepage, 400m downstream from the mine.

A 100  $\mu\text{g/ml}$  standard for full-scale deflection gives steady, drift free readings, and allows straightforward determination of 0.5g samples in excess of 100 ppm. A little extra care is required to reduce that level to 20 ppm.

#### 5.3.3.2. Comparison with other techniques.

Eleven samples were chosen to represent a range of concentrations and digested by a potassium hydroxide fusion technique used for "total" As. (James, 1957, p.233). This method was followed, up to and including, step 6. The sample leaches were then determined, along with 3 blanks, by AAS. Figure 5.13 shows the 9 samples which were above a 50 ppm detection limit, plotted against their equivalent values by nitric acid digestion. The calculated linear regression line is also shown. The figure demonstrates that a nitric acid digestion was more rigorous than a fusion, by a fairly constant factor of 6.6 (reciprocal of slope of regression line).



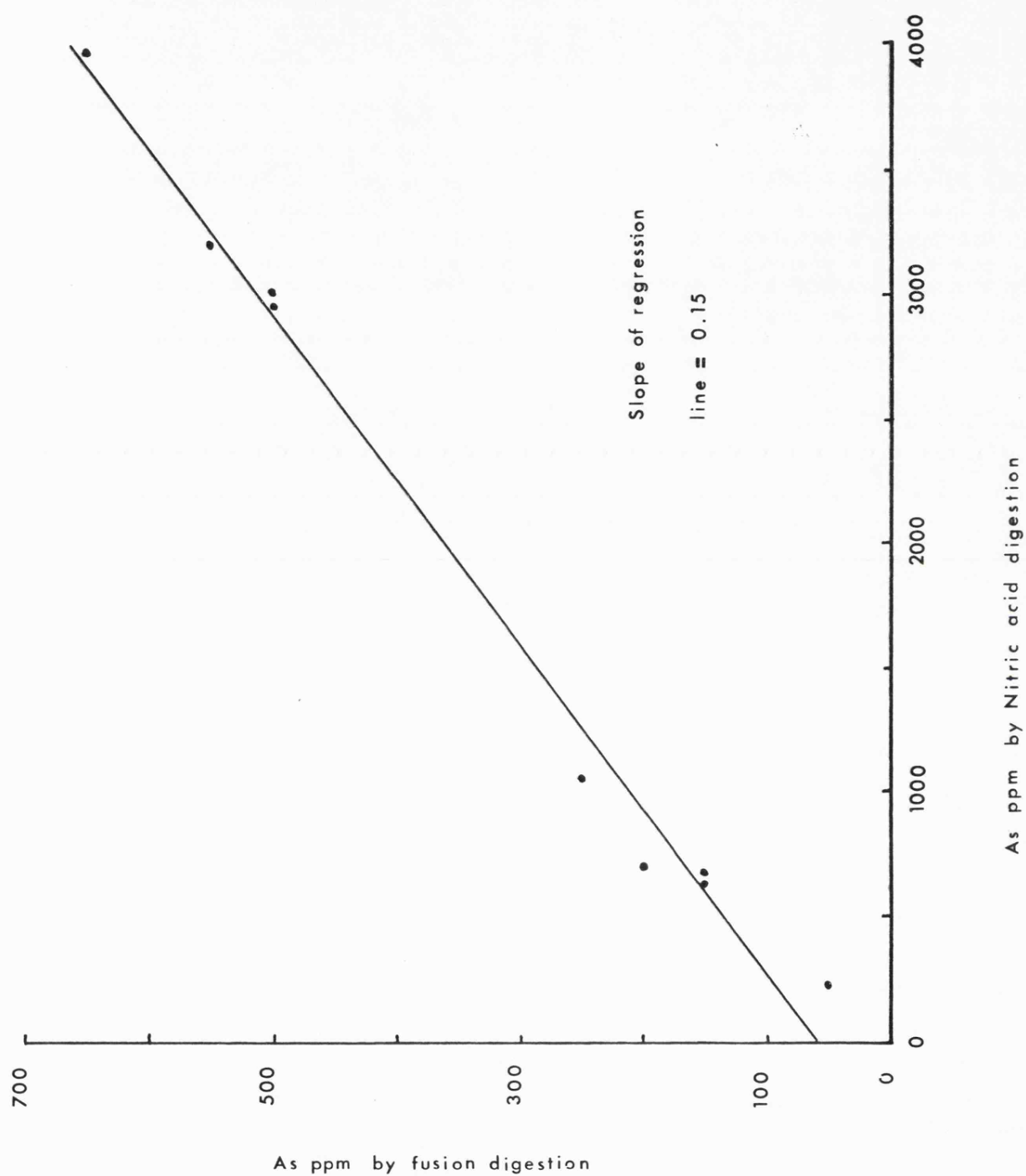


Fig 5.13      Comparison of As results by Nitric acid and by  
fusion digestions.

A cold extraction technique for As determination (James op.cit) was also tried. A 0.25g sample weight was found to be too high for detection in all but one case, and reductions of sample weight to 0.05g and 0.02g were made. The results are tabulated in Table 5.17. The standard series for this method ranges from colourless through yellow to pale brown on mercuric chloride paper in the gutzeit apparatus. In most cases, even at 0.02g sample weight, the colour of the spot was darker than the highest standard. The degree by which an individual paper exceeded the highest standard is indicated in the Table by asterisks. The general pattern confirmed the nitric acid results, which seem to be higher by a factor of at least 5, and probably considerably more.

#### 5.3.3.3. Chemical nature of As at Yarner Wood.

A close correlation exists between Fe and As, (see Chapter 8, Section 8.2.5) in the samples for Yarner Wood, and it seems likely that As in solution, entering a stream which contains an excess of ferric iron, might be expected to form ferric arsenate.

An indirect method of checking this hypothesis came to light following the digestion of selected sediment samples from Yarner Wood in a 10% (w/v) solution of ammonium citrate and hydroxylammonium chloride, a digestion commonly used to determine cold extractable base metals. Analysis of these samples for As proved to be impossible as all samples were below the instrumental detection limit, at that time 20 ppm. It therefore seems likely that the chemical form in which the As occurs is insoluble in the cold extraction leach, but is soluble in nitric acid.

Ferric arsenate was made in the laboratory by filtering the precipitate formed after mixing sodium arsenate and ferric sulphate solutions. The resultant yellow precipitate proved to be readily soluble in nitric acid, but insoluble in 10% ammonium citrate/hydroxylammonium chloride solution.

**TABLE 5.17** Comparison of As results by nitric acid digestion and by cold extraction using gutzeit apparatus.

<u>Sample No.</u>	<u>Nitric acid digestion</u>	<u>CX 0.25g</u>	<u>CX 0.05g</u>	<u>CX 0.02g</u>
8	2340	**	240	*
9	680	*	240	ND
10	3980	***	*	*
12	3220	***	*	*
14	3600	***	*	*
16	8200	**	**	**
17	3580	***	240	*
19	2460	***	*	**
23	3500	***	*	**
26	1880	**	120	*
27	10900	***	**	*
30	2100	***	240	*
33	2480	**	160	**
43	900	***	160	*
57	2400	***	*	*
60	3480	***	*	*
62	520	*	80	115
63	14300	***	**	*
64	200	48	40	50
69	440	*	50	95

All values in ppm.

\*, \*\*, \*\*\* indicate degree by which colour exceeds the highest standard.

#### 5.3.3.4. Conclusions.

High levels of As, up to 2.35%, were reported in samples from Yarner Wood, digested in 4M nitric acid. Samples digested by a potassium hydroxide fusion show good linear correlation with the nitric acid results, but at a level approximately 6.5 times lower. A cold extractable As technique, involving the gutzeit apparatus, was used, and the results

are at least 5 times lower than for nitric acid. However, evaluation of the CX technique was complicated by the high levels of As present in the samples, most of which were beyond the highest gutzeit standard, even when using only 0.02g of sample.

Good correlation between As and Fe results suggests that the As may be present in the sediment as ferric arsenate. Samples prepared using a base metal cold extraction leach were all below a 20 ppm detection limit for As, implying that the chemical compound holding the As is soluble in nitric acid but insoluble in the CX leach. Freshly prepared ferric arsenate exhibits these properties, being readily soluble in nitric acid, but not in 10% ammonium citrate/hydroxylammonium chloride solution.

Ferric hydroxide is a common precipitate in streams in temperate climates, and its proven ability to form ferric arsenate, which is soluble in nitric acid, has useful implications to applied geochemistry. It allows As to be readily determined by AAS using the same leach as that recommended for many other elements, and removes the necessity for fusion digestions and gutzeit apparatus where AAS facilities are available.

#### 5.3.4. Spectral interferences between Ag and Cu

##### 5.3.4.1. Introduction.

Silver was determined in Yarner Wood samples by AAS, using Ag - Cr - Cu - Ni multi-element, hollow cathode discharge lamp. The standard conditions recommended in the Perkin Elmer methods manual were adopted, using a wavelength setting of 328 nm and a slit width of 0.7 nm.

During interpretation of the results, a most striking feature was the very close correspondence between the Cu and Ag results (see for example Figs. 5.14 and 5.15). Whilst one might expect some degree of similarity if the metals are primarily dispersed in a similar way, and respond similarly to the secondary environment, such very close correspondence raised suspicions about possible interferences between the two elements.

#### 5.3.4.2. Examination of Ag analytical procedure.

The first proof that some degree of interference was taking place came when, at the end of a routine run of samples for Ag, the 20  $\mu\text{g/ml}$  Cu standard was aspirated, and gave a reading of 30 units on scale, corresponding to a silver content of about 0.7  $\mu\text{g/ml}$ . This prompted a detailed examination of the lamp output spectrum and the instrument's response to standard Ag and Cu solutions at various wavelengths, and various slit widths.

Firstly, a scan was made of the lamp energy output between 325.0 and 329.0 nm in 0.2 nm intervals at an 0.7 nm slit width. This revealed a single broad peak in energy output, centred on 327.8 nm. This same scan was then repeated twice on the concentration mode of the instrument, once aspirating a 20  $\mu\text{g/ml}$  Cu standard, and once aspirating a 2  $\mu\text{g/ml}$  Ag standard. The results of these scans are shown in Figure 5.16. At 325.0 nm the response is due to the high wavelength end of the 324.7 nm Cu resonance line, and the energy maximum at 327.8 nm is, in fact, the combined peaks of the 327.4 nm Cu, and the 328.1 nm Ag resonance lines. Therefore, adopting the normal, recommended practice for setting the instrument, the wavelength selector

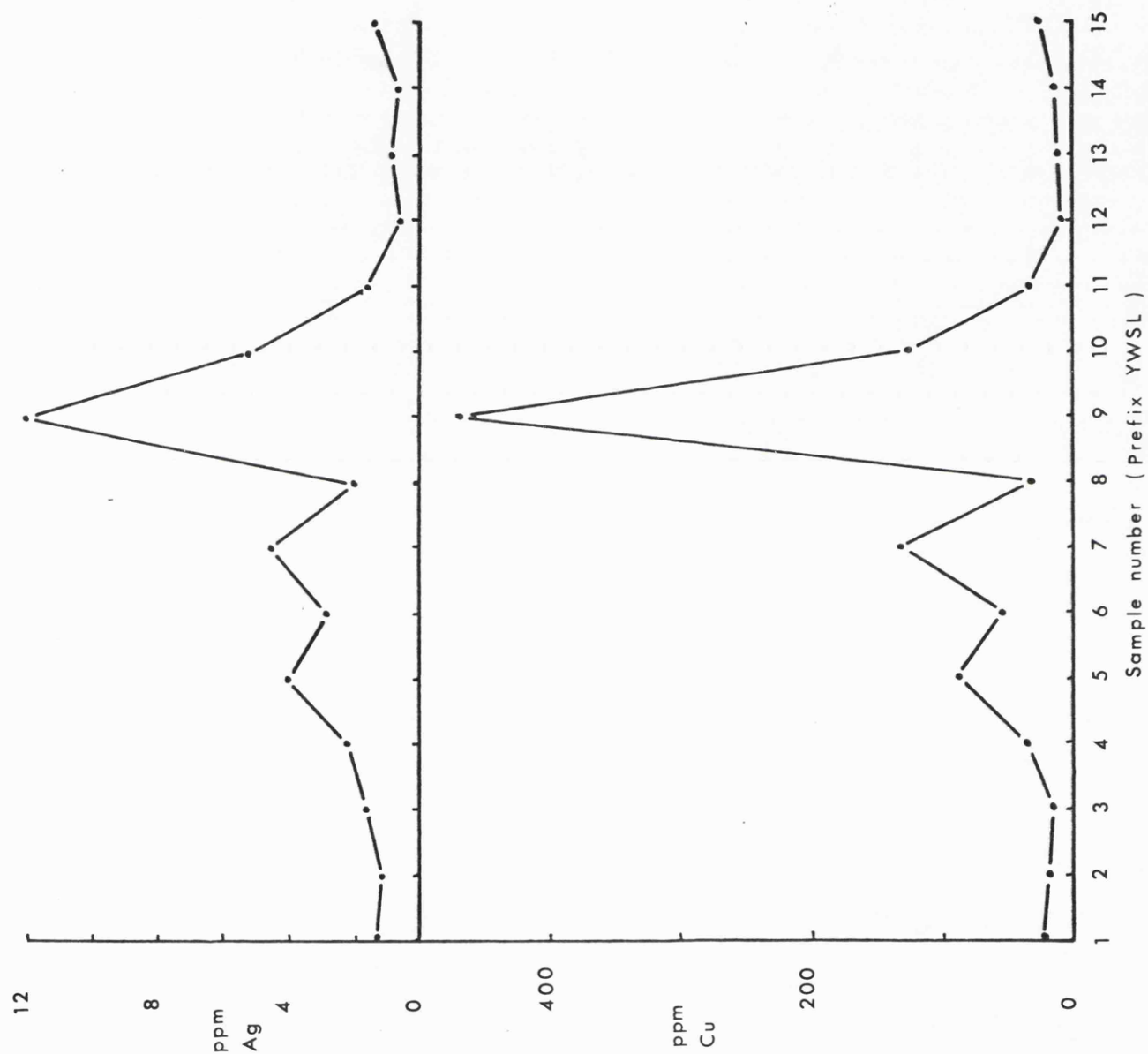


Fig 5.14

Cu and Ag results from soil traverse, Yarnier Wood.

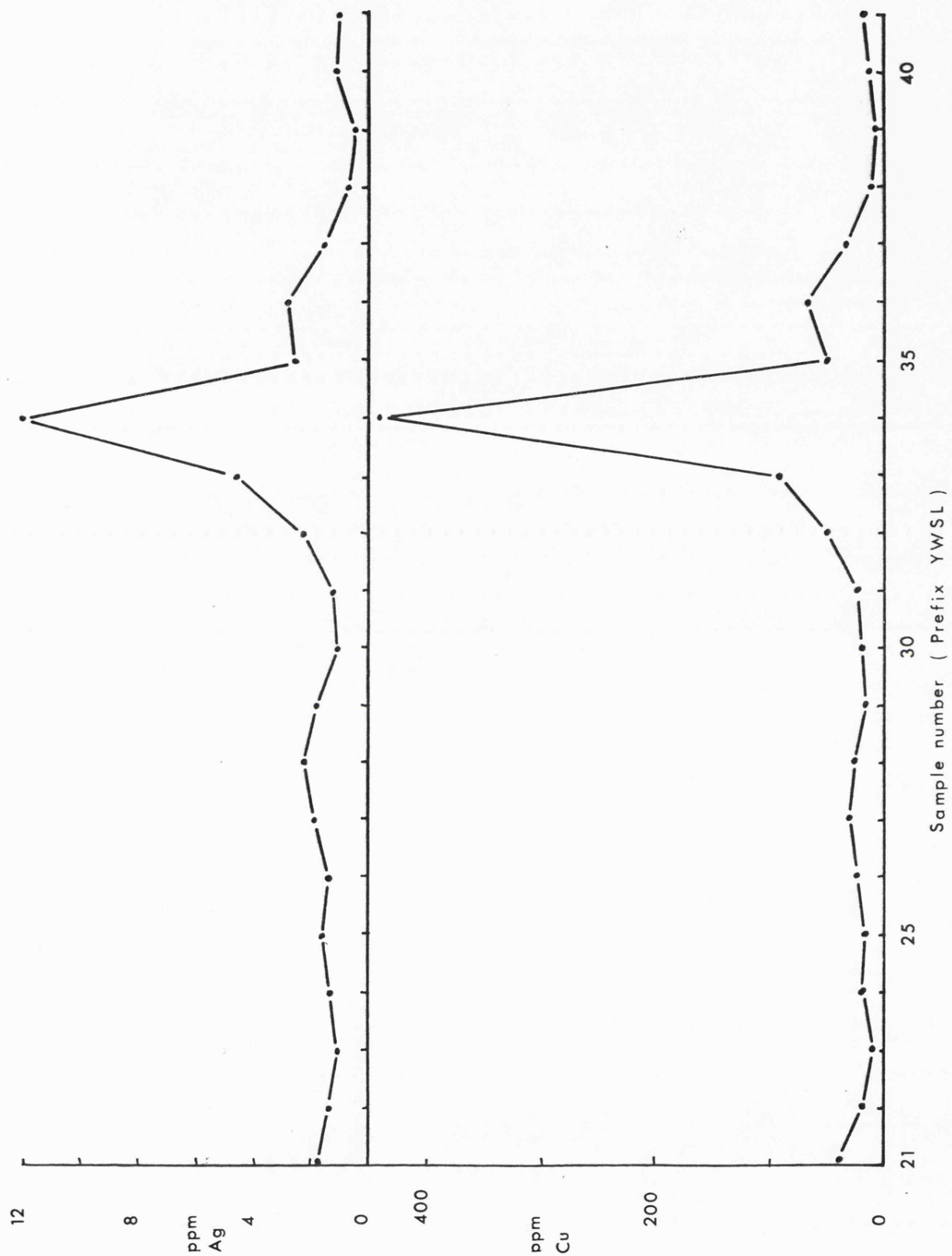


Fig. 5.15

Cu and Ag results from soil traverse, Yarner Wood.

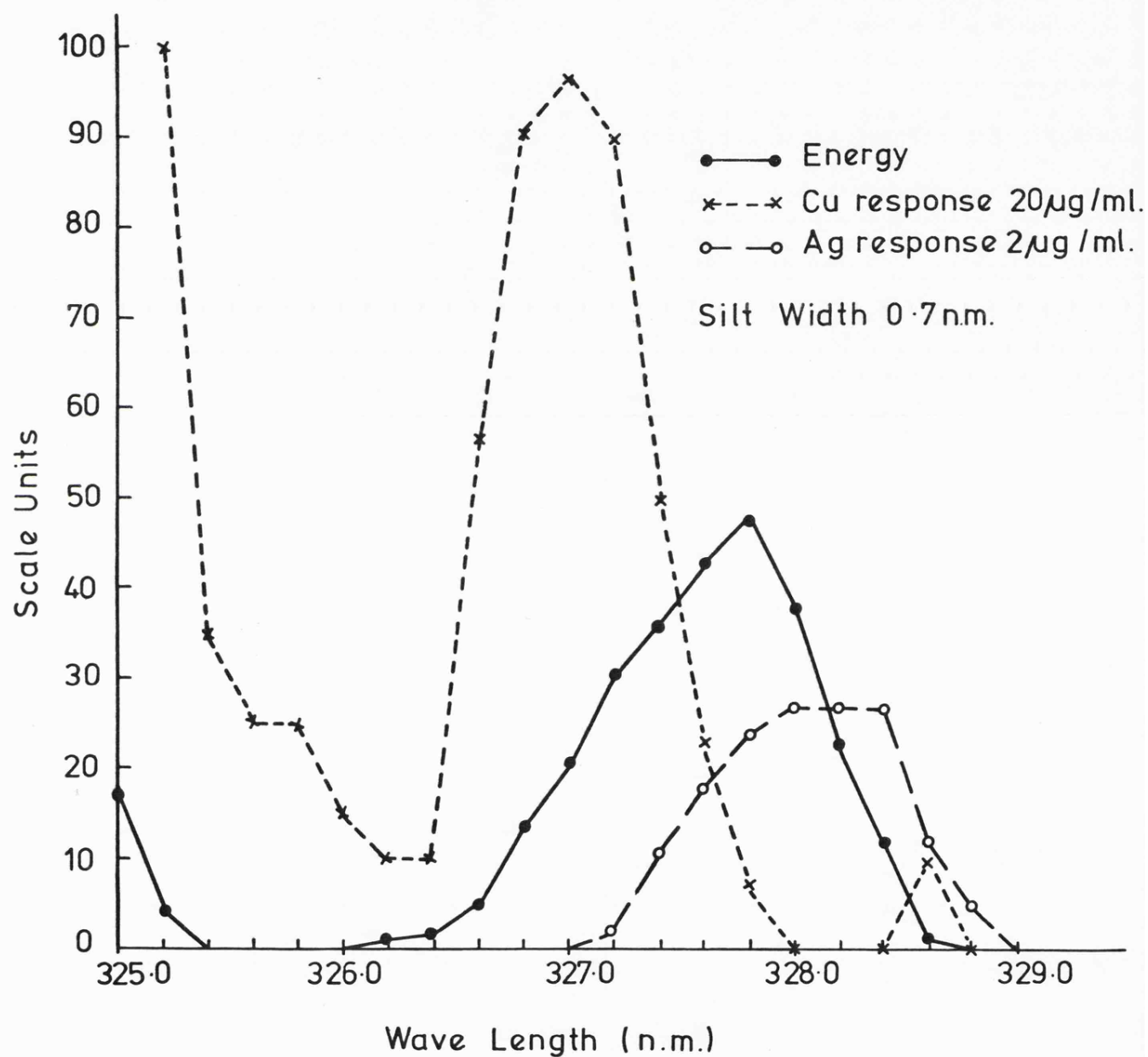


FIG. 5.16 SCANS FOR ENERGY, Cu & Ag USING MULTI-ELEMENT LAMP & 0.7 n.m. SILT WIDTH.



will be set at maximum energy, i.e. 327.8 nm, at which point a 20- $\mu$ g/ml Cu concentration gives a response equivalent to about 0.7  $\mu$ g/ml pure Ag. If, however, the maximum silver response on concentration mode is used to set the instrument, the flat portion of the Ag curve between 328.0 and 328.4 nm can be utilized, and this is free from interference by Cu.

The same scanning procedure was then followed using the 0.2 nm slit width, and using 0.1 nm intervals between 326.8 and 328.2 nm. The results are shown in Figure 5.17. The smaller slit width resolves the two resonance lines quite clearly, showing peaks at 327.2 nm for Cu and 327.9 nm for Ag. The response curves for the individual elements are also much clearer on the smaller slit width, there being no measurable Cu response at 327.6 nm, and only a slight rise in the Cu response at 328.1 nm, (a high point in the Ag response).

#### 5.3.4.3. Conclusions.

The extremely close correlation of the results for Ag and Cu in samples from the Yarner Wood area led to an examination of the energy output spectrum of a Ag - Cr - Cu - Ni multi-element hollow cathode discharge lamp. At the 0.7 nm slit width recommended by the manufacturer the 327.4 nm Cu resonance line is indistinguishable from the 328.1 nm Ag line, and following the optimisation procedures on energy mode, as suggested in the methods manual, will result in selection of too low a wavelength when determining Ag, giving rise to appreciable Cu interference. Thus, the shape of any prominent Cu dispersion pattern will be superimposed upon the Ag results for a given set of samples.

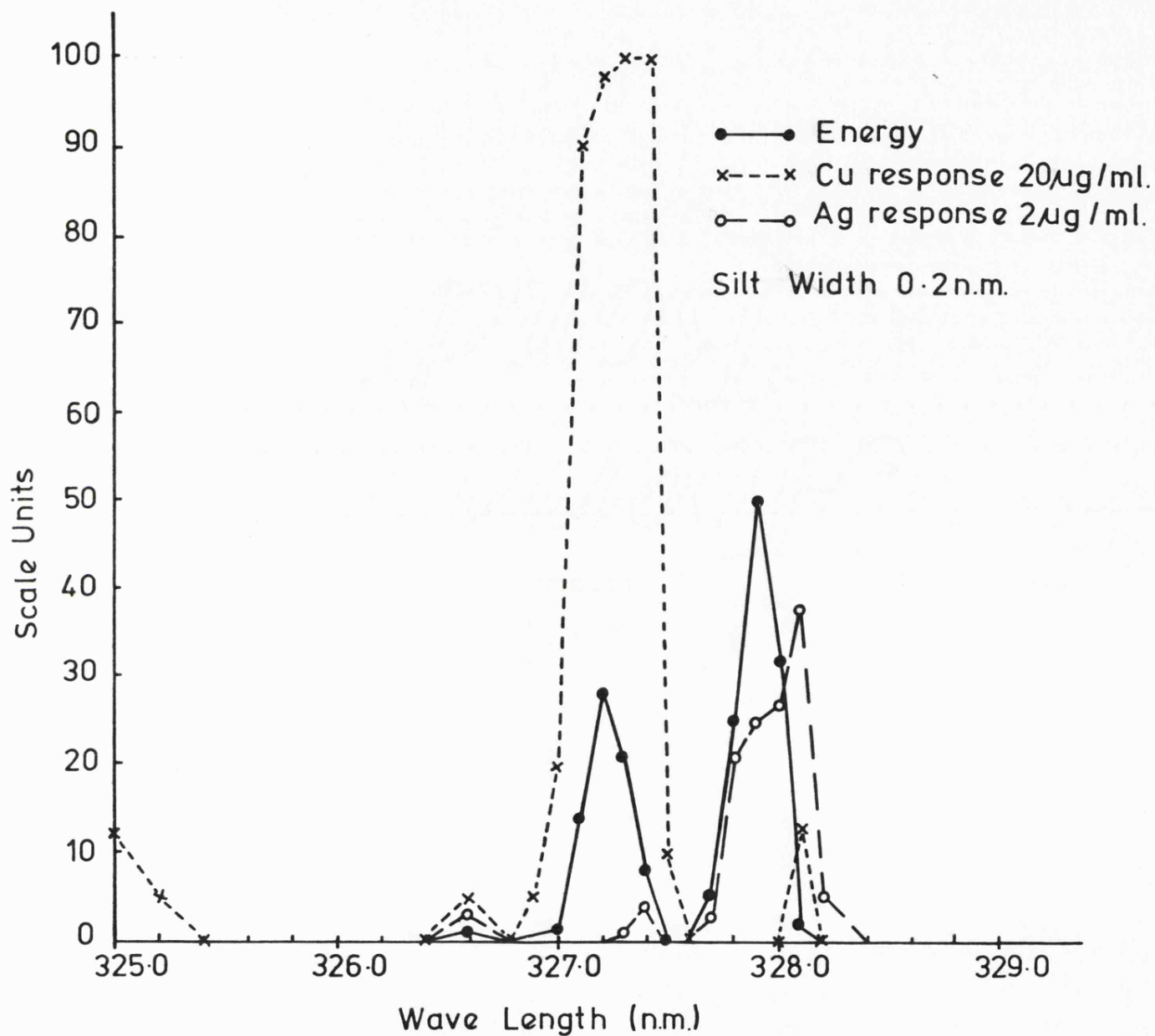


FIG.5.17 SCANS FOR ENERGY, Cu & Ag USING MULTI-ELEMENT LAMP & 0.2 n.m. SILT WIDTH.

This interference may be overcome by using an alternative Ag resonance line, for example, 338.3 nm, which causes a drop in sensitivity. The 328.1 nm line may be utilized, however, once it is established that the wavelength has been set on the silver maximum, and not on the combined Cu - Ag maximum. Wavelength selection for Ag may thus be carried out on the 0.7 nm slit by optimising the silver response on concentration mode, or by wavelength optimisation on energy mode on an 0.2 nm slit, and then reverting to the recommended 0.7 nm slit. In both cases, a direct check on Cu response is an advisable precaution.

Similar precautions are necessary if it is proposed to analyse for Cu on the 327.4 nm resonance line, since interference from Ag will occur if significant quantities of silver are present in the sample. A more serious consequence of selecting the energy-maximum wavelength with an 0.7 nm slit width will be that the chosen wavelength is far removed from the optimum Cu response, causing a serious loss of sensitivity. However, the 324.7 nm Cu resonance line is more frequently used because of its extra sensitivity, and this line appears to be interference free.

#### 5.3.5. Determination of Sn.

##### 5.3.5.1. Introduction

Tin was determined during this study generally by the colorimetric method outlined by Stanton (1966, p.81). However, two factors concerning this method will be briefly discussed. Firstly, a successful attempt was made to determine by AAS the Sn concentration of sample leaches produced by the Stanton method, using a hollow cathode discharge lamp and an air/acetylene flame. Secondly, gross discrepancies were noted in Sn content reported when sample weight is varied.

#### 5.3.5.2. Atomic absorption spectrophotometry.

Two batches of samples from Site P were determined for Sn in the normal way as described by Stanton (op. cit.) on the day the digestion took place. One batch was left overnight, and then, along with a second, newly digested batch, of the same samples, they were all subjected to analysis by AAS using a hollow cathode discharge lamp and an air/acetylene flame.

A correlation coefficient of 0.93 resulted from a linear regression on the samples analysed the same day by the two methods. (See Fig. 5.18). The linear regression line has a slope of 0.78, implying that a slight underestimation by AAS of high values may occur. However, the ease of determination by AAS compared with the colorimetric technique, and the good correspondence of results supports the use of AAS on leaches produced by Stanton's method.

The batch of samples which were read by AAS the day following digestion and colorimetric determination are shown compared in Fig. 5.19. The correlation coefficient, 0.88, is again high, but the slope of the linear regression line is 0.68. This suggests that the Sn levels obtained are lower on the samples left overnight, a view which supports the opinion of Stanton (op. cit., p.83) who suggests that samples retained overnight will suffer loss of Sn to the solid phase unless filtered first.

#### 5.3.5.3. Concentration and sample weight.

Table 5.18 demonstrates that the mean Sn concentration reported from the same samples, but different sample weights, show a dramatic fall as sample weight increases. This is not the interference effect described for other elements in Section 5.3.2. because it is present in samples determined both by AAS and by colorimetry. The discrepancy is,

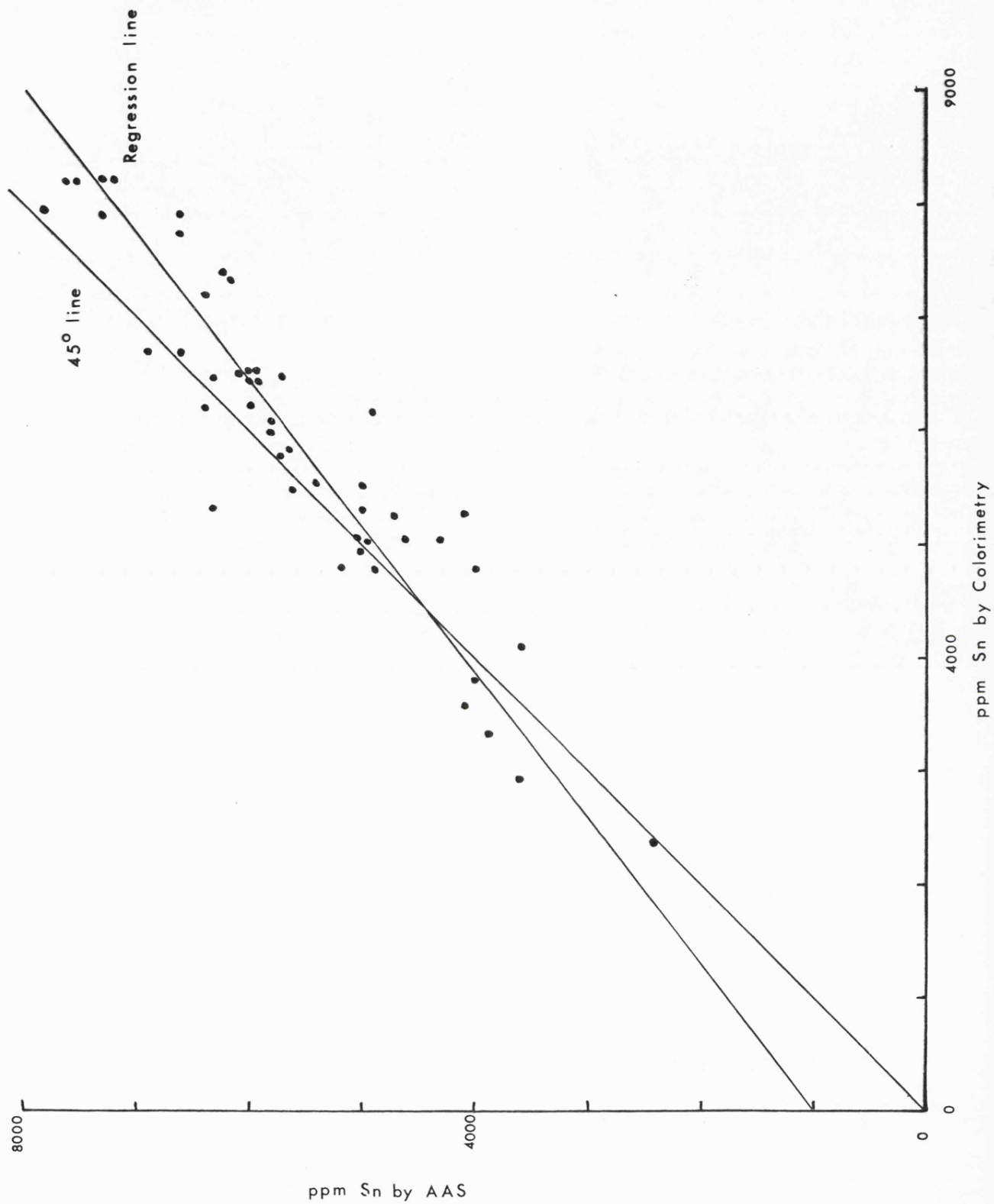


Fig. 5.18

Comparison of Sn results by Colorimetry and  
AAS on the same day.

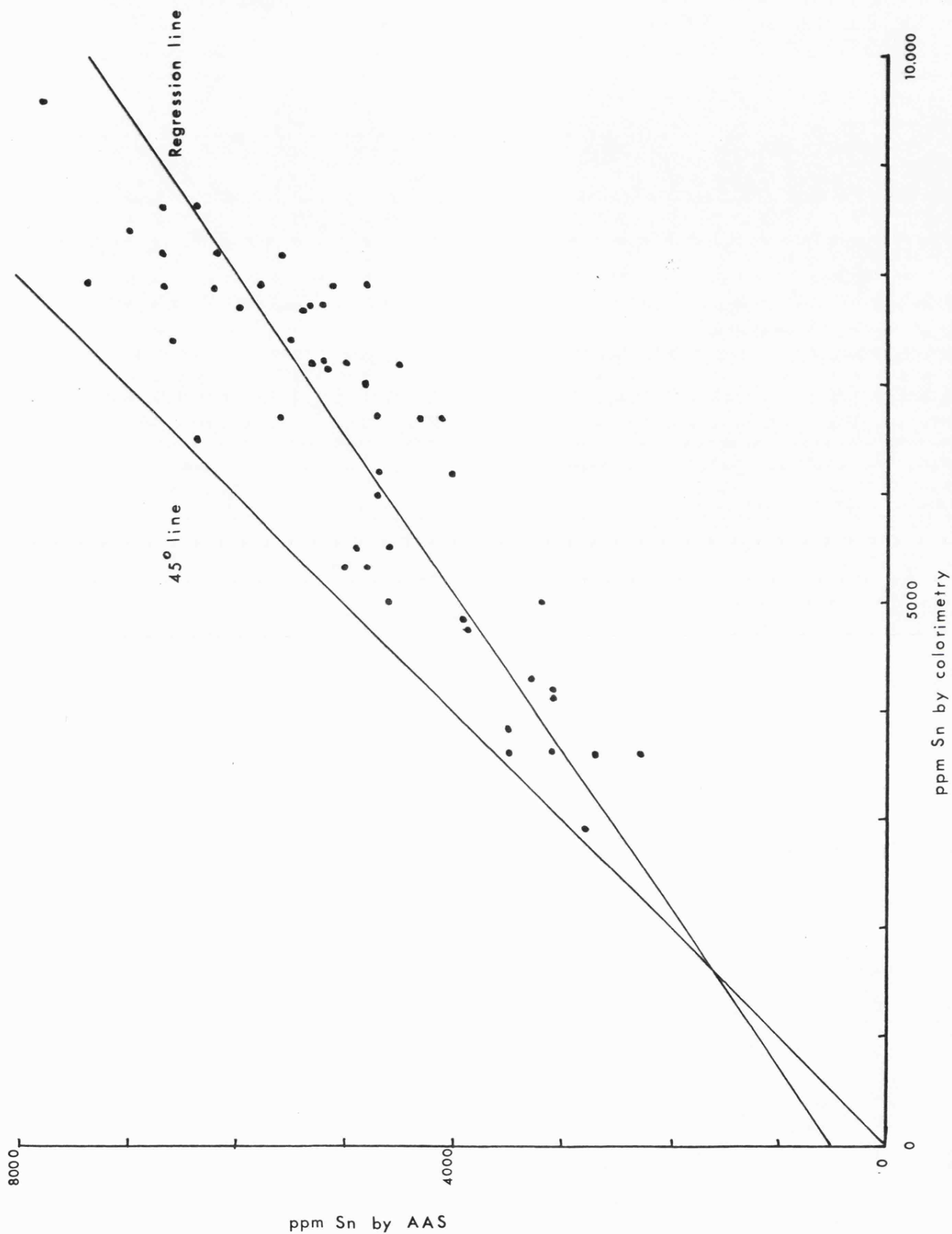


Fig 5.19      Comparison of Sn results by AAS the day  
after by Colorimetry.

**TABLE 5.18** Variation in mean Sn concentration with sample weight  
(all values in ppm).

<u>Sample material</u> (mesh size microns)	<u>Analytical</u> <u>method</u>	<u>0.05g</u>	<u>0.1g</u>	<u>0.2g</u>	<u>0.5g</u>
Site O, -70	Col	134	105	64	48
Site O, -660	Col	136	148	118	82
Site P, -190	AAS	9080	9020	6013	4590
Site P, -660+190	AAS	6320	5150	3667	2814
Site P, -70	AAS	9900	8950	6680	7160
Site P, -190, HEAVY	AAS	40525	39850	18650	6930
Site P, -190+140, HEAVY	AAS	35025	31013	13988	5910

therefore, attributed to inefficiency of digestion and is probably brought about during the heating of samples as a result of sublimation of tin iodide from the top part of the test tube into the atmosphere. It is suggested that heating probably proceeds too rapidly when large sample weights, and consequently large weights of ammonium iodide, are used and that tin iodide is, in fact, driven out of the top of the tubes and lost.

#### 5.3.5.4. Conclusions.

Using smaller weights of sample, i.e. 0.05g or 0.1g, will cause substantial increases in sub-sampling error, especially for a metal like Sn which is often dispersed mechanically as discrete grains in the secondary environment. Longer test tubes, if available, are one possible solution to vapour loss, as are larger flasks rather than test tubes. A further, but time consuming, possibility is to use an 0.5g sub-sample, but sub-divided into say 5 x 0.1g portions for digestion, and then re-combined

when in the liquid phase. The extra time taken during digestion may be made up by the use of AAS rather than colorimetry for determining Sn concentration.

#### 5.4 CONCLUSIONS

Throughout this study, instrumental drift was monitored, using blank and at least two standard solutions. Drift was corrected within every batch of ten samples while residual error after drift correction in the repeat reading of every tenth sample was used to assess instrumental error. Analytical variance was shown to be of similar magnitude for each element, and less than 20% of total error variance for Cu, Pb, Zn, Fe, Mn, As, Co and Ni. The proximity of Cd values to the detection limit has resulted in excessive analytical variance, 86.5% of total error variance, and this renders the Cd results unreliable.

The concept of "aging" of samples, stored before analysis, was investigated, and it has proved difficult to distinguish variance from this source from variations caused by differences in stock solution, especially when new standard stock solutions were made up in the period between analyses. Systematic variations in concentration of dilute standard solutions for Cu and Zn up to 3 weeks, and for Pb up to one week after being made up, were not observed. It is considered unlikely that dilute standards, made up only in small quantities, would be kept for longer periods than this.



Some minor variations in technique, which may occur between sample digestion and analysis, were investigated. Digested samples, stored for more than a few hours before analysis were shown to evaporate and therefore give misleadingly high concentration values. The use of air-tight caps is essential if samples are to be stored in the 10 ml containers used for analysis. Even storage in test tubes may result in misleadingly high readings. However, no chemical interaction between liquid and solid in test tubes was detected when samples were stored, undiluted. Therefore, analysis should follow digestion as quickly as possible. Decanting solutions prior to analysis is desirable to avoid the risk of clogging the nebuliser input tube with solid material, and air-tight lids for sample containers are essential if storage, even overnight, is necessary.

Concentration levels reported from analysing different weights of the same sample are not consistent, a systematic decrease in concentration accompanying increasing sample weight. The types of balance used during weighing are not responsible, nor is the temperature at which samples settle after dilution and homogenization. Less sensitive analytical resonance lines and rotated burner heads on the AAS were investigated, and can also be shown to have no effect on this problem.

The rigour of the acid attack was checked by using various volumes of acid, in two different shapes of container. The pH of sample leaches after digestion was measured directly. The acid retains its concentrated form (pH 0.185) even after digestion of 1.0g sample weights, and the geometry of the digestion vessel was found to make no significant difference. However, during the course of this part of the investigation, it was noted that, for samples diluted to similar matrix concentrations, the discrepancies disappear, and various possible sources of AAS interference were therefore investigated.

Spectral interferences can be discounted for the wide range of elements exhibiting this phenomenon and background interference was also ruled out following studies with a deuterium arc background corrector. Physical interference, caused by differences in sample specific gravity and/or viscosity, were investigated and the differences which exist, determined as insignificant, in the rather crude experiment performed. However, more refined measurement of viscosity might prove to be rewarding.

Consideration of possible chemical sources of interference has shown that the samples dissociate quantitatively in the flame, since the discrepancies are insensitive to height within the flame at which the determination is carried out, and also to the use of the much hotter nitrous oxide/acetylene flame. However, some marginal improvement is achieved by using 0.5% lanthanum chloride solution for dilution, thus removing some potentially interfering anions from the sample matrix.

Non-linear response of AAS for multi-element synthetic samples compared to single element standards was observed, despite the use of electronic curvature correction on the AAS. There appear to be levels above which the linearity is in serious doubt, and it is hoped that further work may provide a better understanding of the problem than the present study.

It remains to be said that samples of different weight may be compared reliably if their matrix concentrations are equated by dilution with weak lanthanum chloride solution. Although systematic, commercial surveys usually adopt a fixed weight of sample, problems may be anticipated from this source when dealing with anomalous samples, and when comparing results of different surveys.

The presence of ferric arsenate in samples from Yarner Wood was indirectly demonstrated. The fact that ferric arsenate is readily soluble in 4M nitric acid renders As easily determined by AAS on leaches from the standard digestion technique adopted. This method was shown to liberate considerably more As than the previously used "total" (i.e. potassium hydroxide fusion) and "cold extraction" techniques, and this higher level of As in the samples facilitates AAS determination (especially when an electrode-less discharge lamp is employed as an energy source).

Spectral interference between the 327.4 nm Cu resonance line and the 328.1 nm Ag resonance line was experienced using a multi-element lamp and the recommended 0.7 nm slit width. Considerable caution should therefore be exercised when setting up for Ag or Cu determinations on these particular resonance lines.

It was shown that AAS with an air/acetylene flame is comparable with colorimetry as a method of determining Sn, following an ammonium iodide digestion. Samples, however, should not be left in contact with the solid residues for any length of time.

Some difficulties were experienced when using an ammonium iodide digestion and especially when the weight of sample taken for analysis was varied. A likely cause of these difficulties is that tin iodide vapour may be lost from the open ends of the test tubes during digestion.

## CHAPTER 6

### WATER AS A SAMPLING MEDIUM

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- 6.2.2. Graphite furnace atomisation
- 6.2.3. Sampling and analytical errors
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#### 6.4 CONCLUSIONS

## CHAPTER 6

### WATER AS A SAMPLING MEDIUM

#### 6.1 INTRODUCTION

Applied geochemical investigations of material from drainage channels are usually confined to the collection and analysis of the stream sediments. However, stream water, when present, forms a complementary system within the drainage regime, and therefore contributes an alternative sampling medium. Furthermore, since both chemical and physico-chemical balances exist between the two, either material, on its own, may provide only incomplete information on the geochemistry of the drainage basin. Indeed, the drainage basin can be seen as a two-phase system (i.e. liquid-solid), in which metal can be transferred, either entirely or in part, from one phase to the other, under varying physico-chemical conditions.

Some metals can be introduced into the drainage channel via the groundwater in solution (see, for example, Horsnail et al., 1969, and Nigrini, 1971). In some cases, precipitation from such solutions may occur under the influence, at least in part, of Eh and pH conditions (see, for example, Hansuld, 1966, and Hem, 1972). Similarly, metals carried into a stream in exchange positions on clays, or in association with other solid-phase material, may subsequently be released into the stream waters by, say, a decrease in the pH of the stream. Thus, a study of the metal contents and physico-chemical conditions of the stream water are an essential pre-requisite to any full understanding of secondary dispersion in the drainage channel environment.

As a sampling medium, water has certain advantages over sediment. Hawkes et al., (1957), point out that, because it is thoroughly mixed, the collection of water samples should be relatively free from sampling errors. However, the very low absolute level of metal, often present in natural waters, means that analytical problems may outweigh this apparent advantage. Data will be presented in this Chapter to support Hawkes et al.'s conclusion. The use of a graphite furnace, rather than a flame, as the means of atomisation in AAS, has allowed detection limits to be lowered substantially and subsequent chapters will discuss the relevance of some results obtained from water analysis.

Contamination is a major hazard when data obtained from natural waters is used in geochemical studies. With metal levels frequently in the nanogrammes per millilitre (i.e. parts per billion)\* rather than microgrammes per millilitre (i.e. parts per million)\* ranges, all forms of contamination must be considered. Contamination derived from sample bottles was investigated, and the bottle tops found to be a potential source of Zn contamination. The purity of concentrated hydrochloric acid, used to acidify samples, was also investigated, as was the use of ultra-pure hydrochloric acid to acidify the samples when collected.

Samples, collected from bulk sample sites B, G and Y, were acidified to varying degrees on collection, whilst alternative samples, to which chloroform was, or was not added, were also obtained. These

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\* Throughout this study, metal content in solution was reported in  $\mu\text{g/ml}$  or  $\text{ng/ml}$  rather than the strictly incorrect approximation of ppm or ppb.

samples were analysed at various times over a two year period. Repeated analysis, over periods ranging from six to nine months of both acidified and not acidified samples collected in Yarner Wood, showed that changes in metal contents do occur over this period, and the reasons for this were investigated. Contamination from suitable sample containers can be shown to be minimal.

## 6.2 ANALYTICAL METHODS AND THEIR CONSEQUENCES

### 6.2.1. Flame atomisation

In the initial stages of this project, only flame atomisation was available at Leicester as an excitation source for use in AAS. Using this technique, Cu, Pb, Zn, Fe and Mn may be detected in some natural waters, although in many samples, (and especially those from background areas) the levels of metal present are below the detection limit of the instrument. With care and experience, it was found that the detection limits outlined in Table 6.1 could be achieved using flame atomisation.

TABLE 6.1: Detection limits achieved by flame atomisation on Perkin Elmer 360 twin beam AAS.

	Cu	Pb	Zn	Fe	Mn
limit (ng/ml)	5.0	50	1.0	10.0	2.5

Note:- These figures represent the concentration represented by a deflection of one scale unit with the instrument on maximum practical sensitivity.

A ten second integration interval was used for water sample determination, each sample being preceded and followed by the determination of an acidified, de-ionised water blank. Although this may appear to be time-consuming when compared with the analysis of higher concentration material, such as sediments or soils, there is, of course, no necessity for any digestion or sample preparation. The water may not even need to

be decanted, and can be aspirated directly into the flame from the sample bottle, provided any sediment present has been allowed to settle.

#### 6.2.2. Graphite furnace atomisation

The availability, after December 1977, of a Perkin Elmer 76B graphite furnace (see Plates 6, 7 and 8), has allowed detection limits for all elements to be very substantially lowered. The furnace has allowed determination of Pb, As and Ni, which were generally undetectable by flame atomisation, and it has also allowed detection of Cu in samples below the flame detection limit. Arsenic was determined by the method proposed by Aruscavage (1977).

As an example, all the samples collected in Yarner Wood were below the detection limit for Pb by flame excitation whereas with the use of the furnace, the concentration represented by one scale unit deflection is only 0.05 ng/ml, (an improvement over the flame technique by a factor of 1000) and a significant pattern emerged in the data (see Chapter 8, Section 8.2.3).

The agreement of results obtained by flame and by furnace was generally good, (see Table 6.2). Allowing for a blank to follow each sample, a little over 20 seconds is required per determination by flame, but between 2 and 3 minutes by furnace, depending on the volume of liquid taken. In addition, the furnace uses more electricity and requires the use of argon as a purge gas. Against this, however, neither acetylene nor compressed air are required. Lamp life is reduced when using a furnace, since the lamp will be on longer for a given number of determinations. Thus, where the concentration of an element is high enough, flame atomisation is preferable because it is quicker and cheaper. A furnace should be used only when concentrations are low, and flame atomisation is too insensitive for the element under consideration.



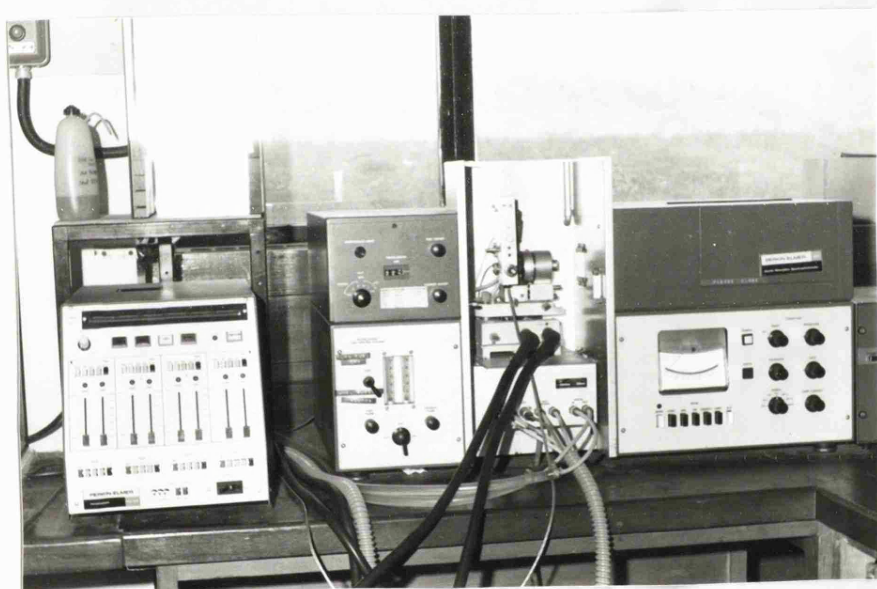


PLATE 6      Perkin Elmer 76B Graphite Furnace, installed in  
360 spectrophotometer.

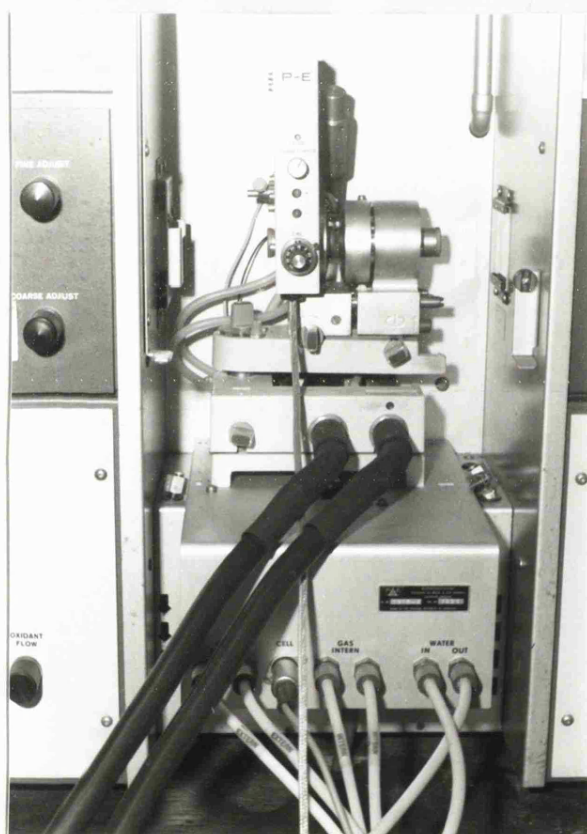


PLATE 7     Perkin Elmer 76B furnace unit.



PLATE 8      Perkin Elmer 76B programmer unit.

**TABLE 6.2:** Comparison of analytical results from Yarner Wood water samples determined for Cu by flame and by furnace excitation.

<u>Sample No.</u>	<u>Concentration from</u> <u>flame</u>	<u>Concentration from</u> <u>furnace</u>
	<u>ng/ml</u>	<u>ng/ml</u>
9/A	b.d.	6
10/A	45	53
12/A	25	60
14/A	30	43
16/A	5	7
17/A	67	69
19/A	10	13
23/A	17	15
26/A	20	27
27/A	b.d.	0.5
27/B	b.d.	b.d.
27/C	b.d.	0.1
27/D	b.d.	0.1
27/E	b.d.	1.3
27/F	b.d.	0.9
28/A	12	10.7
33/A	5	0.3
43/A	b.d.	0.4
46/A	b.d.	5.5
47/A	b.d.	9.0
57/A	b.d.	3.0
58/A	b.d.	4.6
60/A	b.d.	3.6
62/A	b.d.	2.4
63/A	b.d.	4.5
63/B	b.d.	0.05
63/C	b.d.	4.6
63/D	7	0.2
64/A	5	10.5
124/A	b.d.	12.0
125/A	15	16.0
126/A	7	18.0
127/A	b.d.	10.0
128/A	5	13.0

b.d. denotes below detection limit.

All samples prefixed YWW.

### 6.2.3. Sampling and analytical errors

Replicate sampling at certain localities in Yarner Wood has permitted the estimation of combined sampling and analytical variance, (See Section 3.2.2.1, p. 3.3, for the statistical theory) which in this case represents total error variance in the absence of sub-sampling errors. Duplicate analyses, using flame atomisation, have allowed calculation of analytical variance, and both total error variance and analytical variance are shown in Table 6.3. Variances for each element have been compared by computation of F ratios, and the results of these comparisons are shown in Table 6.4. For Cu, analytical variance is actually slightly larger than total error, but the difference is not significant at the 99% confidence level. The differences are not significant even at 90% for Fe and Mn, whilst for Zn, analytical error represents 28% of total error, the remainder being attributed to sampling error. It may thus be concluded that sampling errors are certainly low for water, for 3 out of the 4 elements considered, the total error variance being indistinguishable from the analytical error variance while for Zn the analytical variance constitutes 28% of the total error variance. These data confirm the intuitive conclusion (supported as previously mentioned, by Hawkes et al. (1957)), that water is a relatively homogeneous sampling medium, and not subject to the same high level of sampling error as the sediments.

### 6.2.4. Consequences of analytical capability

Water has advantages over sediment as a geochemical sampling medium in a number of respects. Being homogeneous, and not subject to large sampling errors, water samples may be collected quickly by large numbers of unskilled sampling teams with minimal risk of variable sampling bias. Hawkes et al. (op. cit.) recommend water as a follow-up sampling

**TABLE 6.3:** Total error variance and analytical error variance for water samples for Yarner Wood.

Element	$S_{TE}^2$	$N_1$	$S_A^2$	$N_2$
Cu	$4.63 \times 10^{-4}$	16	$1.88 \times 10^{-3}$	5
Zn	$3.59 \times 10^{-2}$	31	$1.01 \times 10^{-2}$	38
Fe	$7.65 \times 10^{-3}$	32	$7.75 \times 10^{-3}$	2
Mn	$8.51 \times 10^{-3}$	17	$1.65 \times 10^{-2}$	18
Data	$\log_{10}$ transformed.			
$S_{TE}^2$	total error variance			
$S_A^2$	analytical error variance			
$N_1$	number of duplicates used to calculate $S_{TE}^2$			
$N_2$	number of duplicates used to calculate $S_A^2$ .			

**TABLE 6.4:** Comparison of total error and analytical variances.

Element	F ratio	Result
Cu	4.07	SIG at 95%. Not SIG at 99%
Zn	3.54	SIG at 99%
Fe	1.01	Not SIG at 90%
Mn	1.94	Not SIG at 90%

medium, presumably because of difficulties in detecting very low metal concentration in background samples. The development of flame-less atomisation techniques extends the capability of AAS into the range where one may expect to detect even significant background trends in stream waters. A serious drawback to the use of water sampling is that the metal content of stream waters is much more susceptible than sediments to rapid seasonal variations, especially related to changes in rainfall

pattern. (See Huff, 1948, and present study Chapter 7, Section 7.3). On balance it is felt that more use will be made of water sampling as flame-less AAS analytical capabilities become more widely available. The data obtained in this way is likely to be particularly useful in providing a more complete understanding of secondary dispersion in drainage channels, where varying equilibria conditions exist between water and sediment.

### 6.3 WATER SAMPLE COLLECTION

#### 6.3.1. Containers and contamination

Polythene containers are preferable to glass for water sample collection as they are not only less fragile, but also much lighter. For the type of detailed, repeated analysis studies contemplated for this project, 250 ml samples were collected, but in a routine survey situation 100 ml or even 50 ml samples are likely to be adequate.

The polythene sample bottles chosen for this work were firstly washed out with 100 ml of 25% (v/v) HCl. These washings were analysed for Zn by flame atomised AAS. Five of the 40 bottles tested contributed in excess of 100  $\mu\text{g}$  of Zn (i.e. washings greater than 1  $\mu\text{g}/\text{ml}$ ). Only half the forty bottles contributed less than 10  $\mu\text{g}$  Zn. It was noted that drops of liquid clinging to the necks of the bottles, when aspirated on their own, showed high concentrations of Zn, and this prompted a closer examination of the "bakelite" caps used to seal the bottles. Bottles which had recorded low Zn levels proved to be ones with cardboard pads inside the caps, whereas caps with rubber sealing pads gave very high Zn values. Attempts to remove the contaminating sealing pads were not wholly successful, the strength of the glue often causing the cap to break before the pad became free. Therefore, it was decided that, as a matter of routine, a layer of plastic sheeting,

cut from a polythene bag or similar sheeted plastic, should be placed over the neck of each sample bottle to form a seal between liquid and cap. The bottles were washed out twice with de-ionised water, and the metal content of the second set of washings was found to be generally indistinguishable from de-ionised water blanks.

Seven separate Winchesters of Analar Reagent grade concentrated HCl were analysed for Zn and Fe and the amount of contamination caused in 250 ml of water by addition of 0.1 ml concentrated acid calculated; 0.1 ml conc. acid per 250 ml being sufficient to reduce pH below 2.0. Results for this examination are shown in Table 6.5, and demonstrate that, for Zn, contamination is small, whilst for Fe it is variable from batch to batch, and may be quite large, (i.e. in excess of 5 ng/ml in the case of batch 2). Ultra-pure acid, available at a premium price of approximately £13 per litre, was analysed, and for both Fe and Zn the results were below flame detection limits. Thus, unless otherwise stated, ultra-pure concentrated acid was used for acidifying water samples at a concentration of approximately 0.1ml acid per 250 ml water.

#### 6.3.2. Water samples - bulk sample sites B, G and Y

Water samples were collected at bulk sample sites B, G and Y in the autumn of 1975, (see Fig. 1.1) and within a few days of the collection of the bulk sediment samples themselves. At each site eight 500 ml bottles were filled, one without additive, four with 20 ml chloroform to inhibit any organic activity, and two each with 20 ml of 25%, 10% and 5% Analar Reagent grade HCl. Thus the water in three of the bottles contained chloroform and acid, 3 acid alone, one chloroform alone, and one no additive at all. These samples were analysed for Cu, Pb and Zn the day after collection and thereafter at various intervals



**TABLE 6.5:** Degree of contamination caused by adding 0.1 ml AR conc. HCl to a 250 ml water sample

Acid batch no.	Contamination		Contamination	
	ng/ml	Fe	ng/ml	Zn
1		0.9		0.1
2		5.2		0.1
3		0.7		0.1
4		1.7		0.2
5		0.2		0.2
6		1.9		0.3
7		0.2		0.3

for the next 23 months on the following dates:

21st October 1975

25th October 1975

29th October 1975

31st October 1975

4th November 1975

6th November 1975

19th November 1975

8th December 1975

18th February 1976

15th March 1976

13th April 1976

17th January 1977

5th September 1977.

The diluted acids used as additives were also stored and analysed each time with the samples.

#### 6.3.2.1. Results for Zn

Only the samples collected at site G, which is very close to old base metal mine workings, contained appreciable quantities of Zn. These eight samples were all in the region of 1  $\mu\text{g/ml}$  when first analysed, and remained so for the 23 month period over which analyses were carried out. The mean value of the eight samples varied between 901 ng/ml on 18th February 1976 and 1119 ng/ml on 17th January 1977. There was no systematic change in Zn content with time.

Mean and variance values of the thirteen analyses for each sample were calculated, the largest and smallest variances of the eight being compared by an F ratio test. At this sample site it was found that the variation in Zn values between the eight samples (i.e. between-treatments variance) was not significant at the 95% confidence level. A t test was applied to the difference between the largest and smallest means, and this difference was also not significant at the 95% level. It seems, therefore, that the addition of the various additives had no effect on the Zn content of water from this locality.

The results of analyses of the samples from sites B and Y showed that the Zn levels present in these samples were very low (generally less than 10 ng/ml) with the exception of sample 5 from site B which appears to have been contaminated at collection, since it recorded significant amounts of Zn each time it was analysed. The other samples showed no systematic variation in metal content, implying both that the additives made no significant difference, and that no contamination was being introduced from the containers.

#### 6.2.3.2. Results for Cu.

Samples from Site B were surprisingly low in Cu, considering the proximity of Cu-bearing mineralisation. Between one and three months after collection, some contamination was recorded in both samples 3 and 4, and especially in 4, which, 15 months after collection, had risen from below detection limit, to 800 ng/ml.

Samples from Site G had low initial Cu contents, averaging for the first analysis, 20 ng/ml. This apparent content remained fairly constant over the whole analytical period, and there appears to be no systematic difference caused by the various additives.

Samples from Site Y varied from an average for the eight of 20 ng/ml maximum the day after collection, to a minimum of 4 ng/ml one week later, and fluctuated between these two values over the rest of the period under consideration. No systematic effect attributable to the various additives was detected.

#### 6.3.2.3. Results for Pb.

Results for Pb were most disappointing, since almost all samples were below, or very close to, the detection limit. This is not altogether surprising, as AAS analysis for Pb, by flame atomisation, is by no means as sensitive as for Cu or Zn. No systematic pattern can be detected in the samples from any of the three sites. This does at least imply that large scale contamination from the containers did not take place.

#### 6.3.3. Water Samples - Yarner Wood, not acidified

On April 4th 1977, a set of 15 water samples, all prefixed YWW, were collected in Yarner Wood National Nature Reserve, at localities YW 8,9,10,16,17,24,27,28,33,45,60,62,63,64 and 69 (see Fig. 1.2 for

locality references). On the strength of the results described in Section 6.3.2. concerning additives, nothing was added to these samples, and they were analysed for Cu,Pb,Zn,Fe and Mn. All 15 samples were below the detection limit for Pb, and further discussion in this section will relate to the Cu,Zn,Fe and Mn results. Analysis was first carried out ten days after sample collection, that is on April 14th 1977, and subsequently on:

April 22nd 1977,  
April 29th 1977,  
May 12th 1977,  
May 25th 1977,  
July 18th 1977,  
September 5th 1977,  
September 29th 1977,  
November 7th 1977 and  
January 23rd 1978.

Samples were not filtered when collected, but every effort was made to exclude solid material from the bottles. However, it was noted that many of the samples, within a few days of collection, had varying amounts of a flocculent, orange precipitate on the bottom of the bottles. Prior to analysis on November 7th 1977, two samples, YWW 17 and YWW 27, were acidified with 0.1 ml of ultra-pure concentrated HCl, which caused the orange precipitate to dissolve.

#### 6.3.3.1. Results for Mn.

Results from repeated analysis for Mn, over a nine month period, are shown in Table 6.6 which reveals three important features. Firstly, the Mn content of two of the samples, numbers 27 and 63, fall rapidly from high values 6 weeks after collection to very low values 7 weeks later. Sample 24 seems to show a somewhat similar trend but at a much lower level of concentration. The second point of interest is that other samples, notably 10 and 17, which contained modest

concentrations of  $Mn$ , retained their  $Mn$  content throughout the full nine month period. Thirdly, acidification of sample 27 brought the "lost"  $Mn$  back into solution, whilst acidification of sample 17 had no significant effect.

It therefore seems that the samples from Yarner Wood acted in different ways. A gradual change in pH and/or Eh between 6 and 13 weeks after collection may have caused precipitation of  $Mn$  in the two very concentrated samples, 27 and 63, and perhaps also in number 24, whilst the other samples, notably 10 and 17, remained unaffected by this process.

#### 6.3.3.2. Results for Fe.

By the time these samples were first analysed, most bottles had some orange precipitate on the bottom, while others, for example 27 and 63, had appreciable amounts. The most important feature of the Fe results, shown in Table 6.7, is that the soluble Fe content rose dramatically in samples 17 and 27 after acidification, in the case of sample 27 to in excess of  $10 \mu g/ml$ . Every effort was made in the field, short of filtering, to exclude solid material when collecting samples, and it is believed, therefore, that the water in the stream was near-saturated with soluble Fe, and that this Fe was precipitated as ferric hydroxide inside the sample containers, in the same way that it might have been in the stream. Indeed, a very noticeable feature of the stream was the large amount of flocculent orange precipitate on the stream bed downstream of the mine. (See Plate 3). In this reach of the stream, the measured pH/Eh conditions below the mine (pH average 6.5, Eh average +250 mv) are within the ferric hydroxide stability field shown by Hem (1972, Fig. 4, page 446 ). Lowering the pH to about 2 takes the system

**TABLE 6.6:** Mn content of unacidified water samples from Yarner Wood.  
Collected on April 4th 1977

Sample No.	<u>Dates of analysis</u>									
	<u>14/4/77</u>	<u>22/4</u>	<u>29/4</u>	<u>12/5</u>	<u>25/5</u>	<u>18/7</u>	<u>5/9</u>	<u>29/9</u>	<u>17/11</u>	<u>23/1/78</u>
8	5	10	bd	12	10	20	12	24	19	17
9	7	bd	bd	15	bd	7	bd	5	bd	bd
10	40	32	22	30	20	35	35	30	25	35
16	bd	7	bd	5	bd	bd	bd	6	bd	bd
17	30	32	35	25	27	37	30	27	44*	35*
24	22	25	22	30	12	7	5	7	10	21
27	210	222	205	205	210	bd	2	4	262*	275*
28	bd	2	bd	bd	bd	bd	7	9	17	bd
33	5	bd	bd	bd	bd	bd	5	bd	2	bd
45	bd	bd	bd	12	bd	3	2	bd	bd	bd
60	30	20	bd	bd	bd	bd	bd	bd	bd	6
62	bd	5	bd	bd	bd	bd	bd	10	bd	21
63	590	450	500	525	470	12	bd	7	bd	bd
64	bd	bd	bd	3	bd	bd	10	bd	7	7
69	bd	7	bd	bd	bd	bd	bd	2	bd	bd

All values in ng/ml

All samples prefixed YWW

\* denotes samples acidified on 17 November 1977 with 0.1 m. ultra-pure concentrated HCl.

bd denotes below 2 ng/ml detection limit.

into the  $\text{Fe}^{2+}$  solubility field. The reliability of Eh measurement is discussed in greater detail in Chapter 8, Section 8.2.3.3.

Another feature of the results in Table 6.7 is that, after shaking some sample bottles vigorously, enough finely divided, solid, Fe-rich material was aspirated to cause the high value obtained on September 5th 1977 for sample 63, when compared with data obtained for the unshaken sample on both earlier and later dates.

It may be seen, from the spectacular jumps in Fe content after acidification, that the Fe concentration reported from the first analysis probably bears no systematic relationship to the actual amount of the element present, and that collection of unacidified samples for Fe analysis is not to be recommended.

#### 6.3.3.3. Results for Zn.

Most of the samples shown in Table 6.8 had a constant Zn content with time (see for example, samples 8,10,16,17 and 24) and acidification of sample 17 caused no significant change in the Zn level. However, sample 27 is of particular interest since the Zn content reported fell progressively from an initial 99 ng/ml to 30 ng/ml on May 25th 1977. By mid-July, it had fallen to as low as 5 ng/ml. This behaviour strongly reflects the sharp drop in Mn content over the same period. Acidification of sample 27 brought back into solution even more Zn than was initially recorded, implying that some precipitation of zinc may have already taken place in the ten days between collection and analysis.

The effects of contamination of some samples by Zn, presumably leached from the containers, can be deduced from the slight upward trend with time shown by samples 9,28,45 and 69.

**TABLE 6.7:** Fe content of unacidified water samples from Yarner Wood.  
Collected on April 4th 1977.

Sample No.	<u>Dates of analysis</u>									
	<u>14/4/77</u>	<u>22/4</u>	<u>29/4</u>	<u>12/5</u>	<u>25/5</u>	<u>18/7</u>	<u>5/9</u>	<u>29/9</u>	<u>17/11</u>	<u>23/1/78</u>
8	bd	20	10	30	bd	10	bd	bd	bd	bd
9	bd	bd	bd	20	bd	5	bd	bd	40	10
10	20	50	90	40	10	bd	bd	20	20	bd
16	bd	bd	bd	bd	bd	10	bd	bd	20	30
17	40	50	50	30	bd	10	bd	bd	400*	440*
24	90	110	90	80	40	25	bd	60	bd	bd
27	40	170	30	20	bd	bd	270	ND	11000*	10250*
28	bd	bd	5	bd	bd	bd	bd	bd	bd	30
33	bd	bd	bd	20	bd	15	bd	bd	bd	30
45	bd	bd	bd	bd	bd	15	bd	bd	bd	bd
60	20	30	15	25	bd	5	bd	10	bd	bd
62	bd	bd	bd	15	bd	20	30**	bd	bd	bd
63	30	150	60	20	bd	5	320**	50	bd	bd
64	bd	bd	bd	30	bd	10	bd	20	bd	bd
69	bd	bd	bd	bd	bd	bd	bd	bd	20	bd

All values in ng/ml

All samples prefixed YWW

\* denotes samples acidified on November 17th 1977 with 0.1 ml ultra-pure concentrated HCl.

\*\* denotes sample shaken vigorously prior to analysis

ND denotes not determined.

bd denotes below 5 ng/ml detection limit.



**TABLE 6.8:** Zn content of unacidified water samples from Yarner Wood.  
Collected April 4th 1977.

Sample No.	<u>Dates of analysis</u>									
	<u>14/4/77</u>	<u>22/4</u>	<u>29/4</u>	<u>12/5</u>	<u>25/5</u>	<u>18/7</u>	<u>5/9</u>	<u>29/9</u>	<u>17/11</u>	<u>23/1/78</u>
8	24	22	22	26	24	22	17	27	27	32
9	3	bd	2	4	6	6	2	7	7	17
10	84	84	80	88	80	83	62	75	78	75
16	18	19	23	27	24	25	19	21	22	50
17	74	69	69	74	75	70	56	64	75*	67*
24	54	50	52	61	57	55	42	49	57	50
27	99	69	65	37	30	5	3	4	150*	175*
28	9	3	10	14	16	13	11	16	20	25
33	bd	bd	1	bd	7	3	3	2	5	-
45	bd	1	3	7	8	7	3	8	4	12
60	bd	bd	bd	3	bd	bd	bd	bd	bd	bd
62	bd	bd	bd	6	6	4	2	3	2	bd
63	2	4	2	5	5	bd	bd	bd	bd	bd
64	bd	bd	1	3	bd	2	bd	bd	bd	bd
69	bd	bd	3	4	3	3	3	5	6	6

All values in ng/ml.

All samples prefixed YWW.

\* denotes sample acidified on November 17th 1977 with 0.1 ml ultra-pure concentrated HCl.

bd denotes below 1 ng/ml detection limit.

#### 6.3.3.4. Results for Cu.

Initially only two samples contained detectable quantities of Cu, and of these, sample 10 showed, (Table 6.9), a steady increase in Cu content with time being approximately doubled in Cu content after 9 months. This presumably represents the effects of contamination, Cu being leached from the sample containers.

The amount of Cu in solution did not appear to be markedly affected by the pH of the solution, and this implies that it is not co-precipitated with Fe or Mn, a conclusion that was confirmed by the results of cluster analysis described in Chapter 8, Section 8.2.5.

#### 6.3.3.5. Conclusions - unacidified samples.

Samples which were not kept at low pH gave a completely false impression of the Fe content. Certain samples, for example 27 and 63, showed pronounced precipitation of Mn with time and also of Zn, but other samples seemed to retain their Mn and Zn contents, unchanged, for up to nine months. Slight contamination from sample containers was observed for Zn and also for Cu. Cu, which apparently does not co-precipitate with either iron or manganese in this environment, seemed to be unaffected by changes in pH.

The results of this small-scale investigation imply that samples must be acidified if significant results for Fe are sought. There also appears to be sufficient chemical and/or physico-chemical variation, within the small region sampled, to cause differences in behaviour for Mn and Zn in unacidified samples.

**TABLE 6.9:** Cu content of unacidified water samples from Yarner Wood.  
Collected April 4th 1977.

Sample No.	<u>Dates of analysis</u>									
	<u>14/4/77</u>	<u>22/4</u>	<u>29/4</u>	<u>12/5</u>	<u>25/5</u>	<u>18/7</u>	<u>5/9</u>	<u>29/9</u>	<u>17/11</u>	<u>23/1/78</u>
8	bd	5	bd	15	5	bd	2	10	20	bd
9	bd	bd	bd	bd	bd	bd	10	5	bd	18
10	17	17	20	20	25	25	35	27	35	36
16	bd	bd	bd	bd	bd	bd	5	10	bd	bd
17	20	15	20	25	15	27	25	30	25*	42*
24	bd	bd	5	10	bd	2	5	bd	bd	bd
27	bd	bd	bd	bd	bd	bd	bd	10	bd*	5*
33	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd
45	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd
60	bd	bd	bd	bd	bd	bd	bd	bd	bd	6
62	bd	bd	bd	5	bd	bd	bd	bd	bd	bd
63	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd
64	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd
69	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd

All values in ng/ml.

All samples prefixed YWW.

\* denotes amples acidified on November 17th with 0.1 ml ultra-pure  
concentrated HCL.

bd denotes below 2 µg/ml detection limit.

#### 6.3.4. Water samples - Yarner Wood, acidified

A second set of water samples, mostly acidified in the field with 0.1 ml of ultra-pure concentrated HCl, were collected in Yarner Wood on October 16th 1977. The whole set comprised 34 samples, and their significance in terms of the area as a whole will be discussed in Chapter 8, Section 8.2.3. Tables 6.10, 6.11, 6.12 and 6.13 show the Mn, Fe, Zn and Cu analyses of the fifteen samples, which were chosen to duplicate those described in Section 6.3.3. as closely as possible.

##### 6.3.4.1. Results for Mn.

The results, shown in Table 6.10, demonstrate that little or no change in Mn content took place in the five months during which analyses were carried out, except for falls in concentration for the two unacidified samples, 27/B and 63/B.

Contamination may be responsible for the slight increases in content of samples 62/A and 63/A. On the other hand, this may be due to gradual leaching of metal from suspended solid matter trapped in the bottles when the samples were collected. Huff (1948) recommends filtering as standard practice during water sample collection, but if this effect is caused by not filtering, it is not a serious source of imprecision, provided samples are not stored long before analysis.

##### 6.3.4.2. Results for Fe.

The results for Fe, shown in Table 6.11, are in striking contrast to the confused jumble of results shown in Table 6.7. Apart from the two unacidified samples, which showed the anticipated rapid precipitation of Fe from solution, the results remained stable over the

TABLE 6.10: Mn content of acidified water samples from Yarner Wood.  
Collected on October 16th 1977

<u>Sample No.</u>	<u>Dates of analysis</u>			
	<u>19/10/77</u>	<u>7/11/77</u>	<u>20/1/78</u>	<u>21/3/78</u>
9/A	7	2	bd	bd
10/A	70	55	82	78
16/A	7	7	7	2
17/A	90	95	87	91
23/A	125	135	127	144
27/A	252	242	232	256
27/B*	257	225	232	192
28/A	17	17	30	13
33/A	5	bd	bd	bd
43/A	bd	bd	bd	bd
60/A	132	117	130	125
62/A	bd	bd	9	19
63/A	490	500	555	586
63/B*	317	7	7	26
64/A	55	55	70	58

All values in ng/ml.

All samples prefixed YWW.

\* denotes sample not acidified.

bd denotes below 2 ng/ml detection limit.

**TABLE 6.11:** Fe content of acidified water samples from Yarner Wood.  
Collected on 16th October 1977

Sample No.	<u>Dates of analysis</u>			
	<u>19/10/77</u>	<u>7/11/77</u>	<u>20/1/78</u>	<u>21/3/78</u>
9/A	200	270	270	250
10/A	975	1000	1010	1000
16/A	bd	50	170	150
17/A	1050	970	1010	1025
23/A	2400	2400	2400	2500
27/A	6800	8000	7500	8000
27/B*	300	bd	80	bd
28/A	50	80	60	125
33/A	bd	bd	20	bd
43/A	bd	bd	30	bd
60/A	500	560	630	700
62/A	bd	20	125	75
63/A	3750	4900	4900	4925
63/B*	100	40	10	bd
64/A	250	370	380	375

All values in ng/ml .

All samples prefixed YWW.

\* denotes sample not acidified.

bd denotes below 10 ng/ml detection limit.

five months of storage and analysis. Some slight overall increases, for example in samples 16/A, 28/A, 60/A, 63/A and 64/A, may have been due to contamination, although the persistently low values recorded by samples 33/A and 43/A imply that not all sample containers cause contamination. The accidental inclusion in the samples of some finely divided, suspended, solid material, which was gradually leached of metal by the weak acid sample solution, may in fact be the cause of the observed, slight increases in metal content.

#### 6.3.4.3. Results for Zn.

The Zn results, shown in Table 6.12, were stable over the five month period. Only the two unacidified samples showed particularly fluctuating results. Sample 27/A was, for example, quite stable, whereas its counterpart in Table 6.8 showed a marked and rapid decrease in metal content.

#### 6.3.4.4. Results for Cu.

The results for Cu, shown in Table 6.13, were stable over the five month period. The two unacidified samples were from sources which apparently contained no detectable Cu anyway, and so the effects of acidification cannot be assessed from these particular results.

#### 6.3.4.5. Conclusions - acidified samples.

Variation in metal content of water samples with time after collection, which was a pronounced feature of the Mn and Zn content of some unacidified samples, and the complete lack of pattern of Fe results, were both overcome by the addition of a small amount (0.1 ml per 250 ml sample) of ultra-pure, concentrated HCL. The Cu

**TABLE 6.12:** Zn content of acidified water samples from Yarner Wood.  
Collected on October 16th 1977.

Sample No.	<u>Date of analysis</u>			
	<u>19/10/77</u>	<u>7/11/77</u>	<u>20/1/78</u>	<u>21/3/78</u>
9/A	2	12	10	12
10/A	109	106	120	116
16/A	33	38	37	40
17/A	108	120	122	112
23/A	11	23	30	20
27/A	119	120	127	126
27/B*	104	45	30	30
28/A	27	32	30	20
33/A	bd	1	bd	bd
43/A	bd	4	12	4
60/A	8	9	12	4
62/A	bd	6	12	8
63/A	7	20	17	16
63/B*	6	3	bd	8
64/A	22	34	35	32

All values in ng/ml.

All samples prefixed YWW.

\* denotes sample not acidified

bd denotes below 1 ng/ml detection limit.



**TABLE 6.13:** Cu content of acidified water samples from Yarner Wood.  
Collected October 16th 1977.

<u>Sample No.</u>	<u>Date of analysis</u>			
	<u>19/10/77</u>	<u>7/11/77</u>	<u>20/1/78</u>	<u>21/3/78</u>
9/A	bd	bd	5	5
10/A	45	45	50	52
16/A	5	bd	5	2
17/A	67	65	55	55
23/A	17	20	25	15
27/A	bd	bd	bd	bd
27/B*	bd	bd	bd	bd
28/A	12	bd	5	10
33/A	5	bd	bd	bd
43/A	bd	bd	bd	bd
60/A	bd	bd	10	bd
62/A	bd	bd	bd	bd
63/A	bd	bd	5	bd
63/B*	bd	bd	5	10
64/A	5	15	10	bd

All values in ng/ml.

All samples prefixed YWW.

\* denotes sample not acidified.

bd denotes below 2 ng/ml detection limit.

content of the samples seemed to be unaffected by addition of acid. It is possible that some increase in apparent metal content may have been caused by weak acid samples gradually leaching metal from any suspended, solid matter included in the samples or by gradual contamination from certain sample containers. Every attempt should be made to avoid trapping solid material at the time of collection, although it is doubtful if this effect is of sufficiently large scale to necessitate filtering at the time of collection and both possible causes will be minimised if prolonged storage prior to analysis is not contemplated.

#### 6.4 CONCLUSIONS

Many metals find their way into the stream environment in solution via the groundwater, or direct runoff. A chemical and physico-chemical balance, or equilibrium, may be assumed to exist between stream water and the sediment which it transports. Therefore, any attempt at a full understanding of secondary dispersion patterns should include chemical analysis of, and physico-chemical measurements on, stream water, where present, and in temperate climates it is very unusual for any but the smallest streams to dry out completely.

Analytical sensitivity and reproducibility are common constraints on the use of water as a sampling medium. A Perkin Elmer 360, twin beam, AA spectrophotometer was used with flame atomisation to achieve detection limits of at least 1 ng/ml, 50 ng/ml, 5 ng/ml, 10 ng/ml and 2.5 ng/ml for Zn, Pb, Cu, Fe and Mn respectively. Significant patterns for Zn, Fe and Mn were detected in this way, and samples from close to large Cu sources may also be above detection limits. Use of a Perkin Elmer 76B HGA graphite furnace atomiser lowered detection limits by factors ranging from 100 to 1000. Samples below the flame detection limit for Cu and Pb were determined, and other elements such as As, and Ni, where all the samples available were below flame detection limits,

were satisfactorily determined with the furnace. Comparability between samples detected by flame and by furnace was good, although where flame atomisation is possible, it is desirable from the point of view of speed, convenience and expense. It may thus now be feasible to consider water as a regional sampling medium, since it is possible to detect with a furnace the very small amounts of metal anticipated in background areas, as well as the larger amounts in mineralised regions.

Duplicate sampling and analysis has allowed an investigation of sources of error, which supports the conclusion of Hawkes et al. (1957) that water is a homogeneous sampling medium, and that sampling error is, therefore small. This means that large numbers of unskilled samplers may be used for water sample collection with only minimal risk of introducing variable sampling bias. However, seasonal fluctuations in metal content of stream waters, the subject of part of Chapter 7, present serious drawbacks to the use of water as more than a follow-up method.

An examination of the degree of contamination caused by metal leached from inside the plastic containers used in this study, revealed that the pads used to effect a water-tight seal when the tops are screwed on, can be a major source of contamination, especially if they are made of rubber. Sheets of plastic were placed over the tops of bottles when samples were collected, in order to prevent them coming into contact with contaminating lids.

Seven separate bottles of Analar Reagent grade, concentrated HCl were tested for purity. Detected levels of Zn were found to be very low when considered in terms of the amount necessary to acidify a 250 ml water sample, but some of the acids showed quite high levels of Fe. Ultra pure acid was found to be a considerable improvement and, as it is only

necessary to use 0.1 ml per sample, the extra expense is minimal.

Water samples, collected at bulk sample sites B, G and Y, were spiked with various additives, chloroform, 25%, 10% and 5% analar reagent grade HCl. These samples were analysed for Cu, Pb and Zn at various time-intervals over the following 23 months. The pattern, in those samples which contained detectable amounts of metal, was that the various additives appeared to make no significant, systematic difference, nor did the length of time for which the samples were left.

A set of unacidified water samples were collected in Yarner Wood at Easter 1977, and analysed for Mn, Fe, Cu and Zn at various times over the following nine months. The Fe results showed no systematic change with time, but varying amounts of flocculent, orange precipitate were observed in the sample bottles. This dissolved in two of the samples when they were subsequently acidified, and large amounts of Fe were found to have been released into solution. The hypothesis that the stream water was near-saturated with Fe at its normal pH/Eh conditions, and was actively precipitating ferric hydroxide, is supported by the observed Fe precipitate in the stream, and theoretical considerations of Fe stability at various pH/Eh conditions. Decreases in the Mn and Zn content were noted for two samples, whilst the others remained unaffected over the nine month period. This decrease in observed Mn and Zn was reversed by acidifying the sample. Cu values, where detectable, were unaffected by time or acidification.

As a consequence of these findings, a second set of samples were collected, and all but two were acidified in the field. An apparently significant set of results were obtained for Fe, and repeated analysis over a five month period revealed that no significant changes in Fe content took place.

It, therefore, seems to be advisable to acidify water samples on collection, and that subsequently they may be left for substantial time periods before analysis, provided:

(a) that care is taken to minimise contamination from bottle tops, and:

(b) that the amount of suspended, solid material present in the sample is kept to a minimum.

Notwithstanding the above, if any such changes in metal content are to be avoided, analysis ought to follow sample collection as quickly as possible.

There are some practical disadvantages to acidifying samples in the field. The possibility of contaminating ultra-pure acid must be considered, as must the consequences of spilling concentrated acid into a rucksack or similar carrier-bag. Inaccuracies in pipetting in the field must be contemplated and breakage of delicate pipettes seems almost inevitable. A compromise may, however, be to acidify samples at the end of each day when the samples are returned to the headquarters of the operation. The results from acidification of samples YW 17 and YW 27, given in Tables 6.6, 6.7, 6.8 and 6.9, indicate that precipitated metals were released into solution even when the samples had been stored, unacidified, for 7 months. Therefore, a delay of a few hours, allowing samples to be acidified in the field headquarters, seems to be justified.

## CHAPTER 7

### SEASONAL VARIATIONS IN METAL CONTENT OF STREAM SEDIMENTS AND WATER

#### 7.1 INTRODUCTION

#### 7.2 SEDIMENT SAMPLES

##### 7.2.1. Introduction

##### 7.2.2. Comparison of seasonal and error variance

##### 7.2.3. Results for individual elements

7.2.3.1. Copper

7.2.3.2. Lead

7.2.3.3. Zinc

7.2.3.4. Iron

7.2.3.5. Manganese

7.2.3.6. Arsenic

7.2.3.7. Cadmium

7.2.3.8. Cobalt

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#### 7.3 WATER SAMPLES

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CHAPTER 7SEASONAL VARIATION IN METAL CONTENT OF STREAM SEDIMENT AND WATER7.1 INTRODUCTION

Applied geochemical investigations and particularly regional reconnaissance drainage surveys, are generally accepted as rapid, if somewhat imprecise, methods of mineral exploration. In the context of the type of precision commonly accepted in applied geochemistry, and referred to in Section 2.2.1. (p.2.4), the attitude towards seasonal variation of metal content in stream sediments of such as Hosking (1971) is not altogether surprising. He re-sampled a few localities after a gap of about 18 months, and, finding the Cu values to be similar, concluded that seasonal variations are not large enough to be a cause for concern. However, as techniques in applied geochemistry become more refined, it may be anticipated that obtainable precision levels will improve, and variance, caused by sampling and analytical errors, may be substantially reduced. Some attempts at error reduction have already been described in this thesis, and in view of the precision levels, even now apparently possible, a re-investigation of seasonal variation seems germane. This is especially so since, as Webb et al. (1968) point out, regional stream sediment surveys are now being used not only as a means of locating mineralisation, but also increasingly frequently as a method of regional geochemical mapping. It is also reasonable that a re-investigation of seasonal variations should include analysis of stream waters as well as sediments, in view of the potential, outlined in Chapter 6, for water as a sampling medium.



Huff (1948) recommended that water samples should be collected at times of low run-off, recognising that serious fluctuations in metal content of stream waters may be anticipated following heavy rainfall. Govett (1960) detected substantial seasonal variations in both the total and cold-extractable copper contents of sediments, from what was then Northern Rhodesia, collected at approximately monthly intervals over a period of nearly a year. Considering that such large fluctuations were observed in this tropical climatic environment, it is surprising that this source of variation has not since been taken more seriously. De Grys (1962) collected samples from several rivers in Central Chile every month for a year, and observed seasonal fluctuations in the Cu and Zn content of sediments and the Cu content of waters, which she attributed to changes in climatic conditions. Barr and Hawkes (1963), working in British Columbia, collected sediment samples in two rivers on a weekly basis, and concluded that such seasonal variations as were observable in the copper values, were of a sufficiently small magnitude to be overlooked in the mineral exploration context. More recently similar conclusions were reached by Hoffman and Fletcher (1972) and Chork (1977) from investigations of seasonal variations in stream sediments in temperate latitudes.

Chork (op.cit.) based his evaluation of seasonal variation on two study areas. In one area, he sampled two streams in north west Maine, USA, three times between June and August 1973, and in the other area, two streams in New Brunswick, Canada, were sampled, once in the autumn of 1973 and again in the spring of 1974. De Grys (op.cit.) has demonstrated that seasonal fluctuations commonly have periods of months, and may be correlated with major

climatic fluctuations. However, results based upon sampling at monthly intervals are prone to single high or low values (see for example De Grys, op.cit., Fig. 3) some of which may perhaps be related to error variation, particularly sampling error, rather than seasonal effects. Therefore, the intention, in the design of the present experiment, was that samples should be collected at weekly intervals, and any long period trends interpreted by means of a moving average smoothing technique, which will minimise the effects of error variation.

The availability of trained sample collectors to undertake regular and frequent sampling is an obvious problem, and the author was most fortunate in securing the cooperation of the Nature Conservancy Council, whose resident staff at Yarner Wood National Nature Reserve, near Bovey Tracey, Devon, collected samples, in all weathers, at weekly intervals, over a two year period from April 1976 to April 1978.

For the first year, which included the severe drought of the summer of 1976, sediment samples, prefixed YWS, were collected each week at locality YW8, (see Fig. 1.2 and Plate 9), 10m below the Yarner Stream and Woodcock Stream confluence. From April to October 1977 water samples, prefixed YWWS, were collected weekly at YW10 (see Plate 10) in the Yarner Stream, just above the confluence. These water samples were not acidified on collection. From 15th October 1977 onwards, water samples, still prefixed YWWS, but now acidified, were collected along with sediment samples, prefixed YWWSS, from locality YW10.



PLATE 9      Yarner Stream at locality YW 8.



PLATE 10

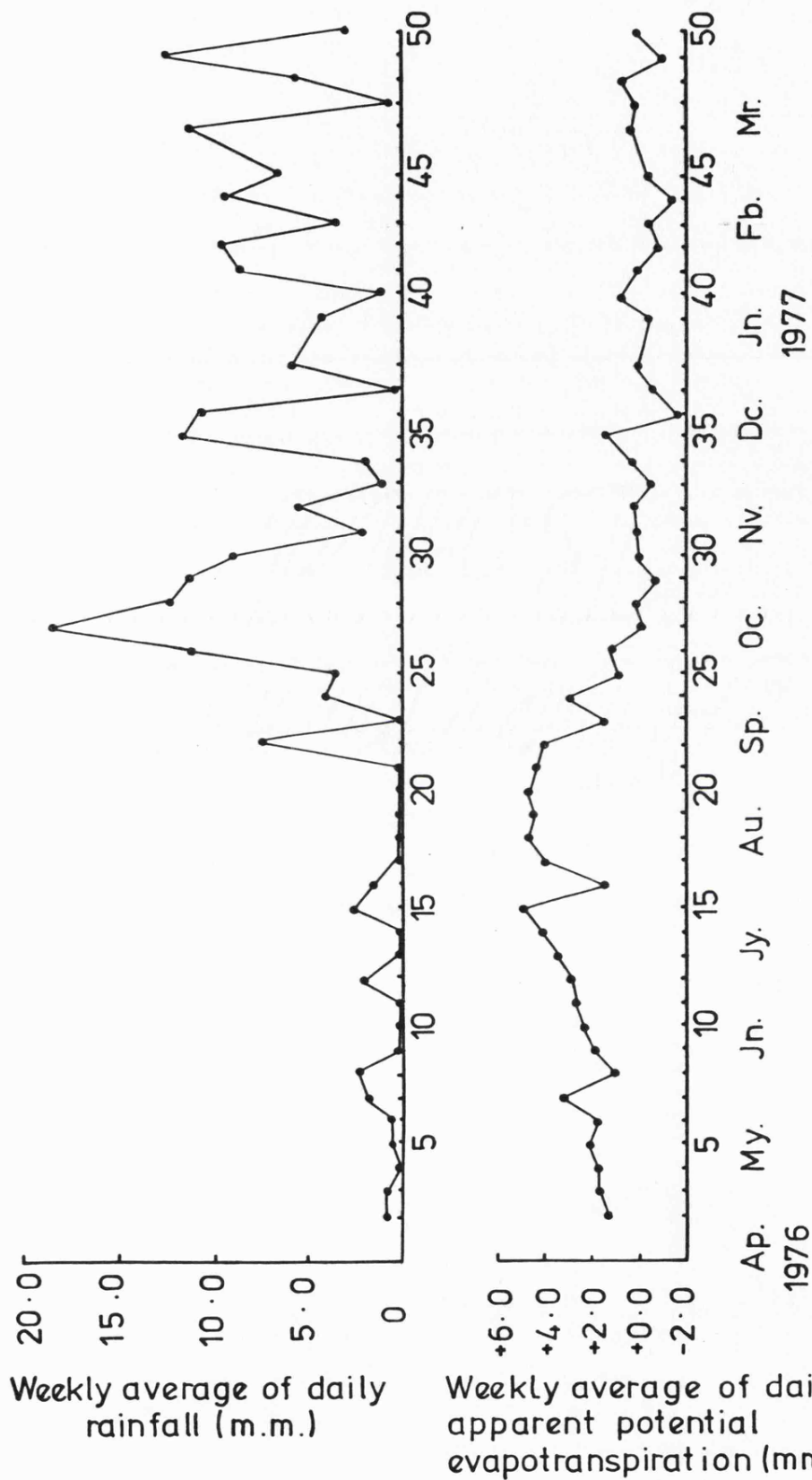
Yarner Stream at locality YW 10.

A well equipped meteorological station is maintained on the Nature Reserve at Yarner Wood, and climatic data from it was supplied by the South West Water Authority. The potential evapotranspiration observations from the irrigated lysimeter at the station were supplied by the Meteorological Office. The climatic factors chosen for comparison with the geochemical data are shown, for the two one year periods, in Figures 7.1 and 7.2. The daily rainfall, computed as a weekly average, was plotted, as was a weekly average of the daily potential evapotranspiration. According to Mather (1974), evapotranspiration, or net water loss from the whole ground surface via evaporation and transpiration, is dependent on net radiation, wind velocity, humidity, soil type and moisture content, vegetation type and depth of rooting, and land management policy. When water loss is not restricted by lack of moisture, i.e. irrigation is used to keep the surface moist, potential evapotranspiration is almost entirely dependent on solar radiation and rainfall. This makes it a potentially useful climatic indicator for the present study, as high values of evapotranspiration characterise warm, dry periods, when the water content of the rivers is derived from the groundwater. Conversely, low values correspond to cold, wet periods when the rivers are fed dominantly by surface run-off.

## 7.2 SEDIMENT SAMPLES

### 7.2.1. Introduction

Samples collected between April 1976 and March 1977 were numbered YWS 1 - 50, and those collected between October 1977 and April 1978, YWWSS 27 - 52. All the samples were analysed by AAS for Cu, Pb, Zn, Fe, Mn, As, Cd, Co and Ni following the digestion of 0.5g of minus 125 micron sample material in 4M HNO<sub>3</sub> for 4 hours



Sample number corresponding to period averaged. ( Samples Yws 1-50 )

FIG. 7-1

EVAPOTRANSPIRATION & RAINFALL THROUGHOUT  
APRIL 1976 - APRIL 1977. CORRESPONDS TO Yws 1-50



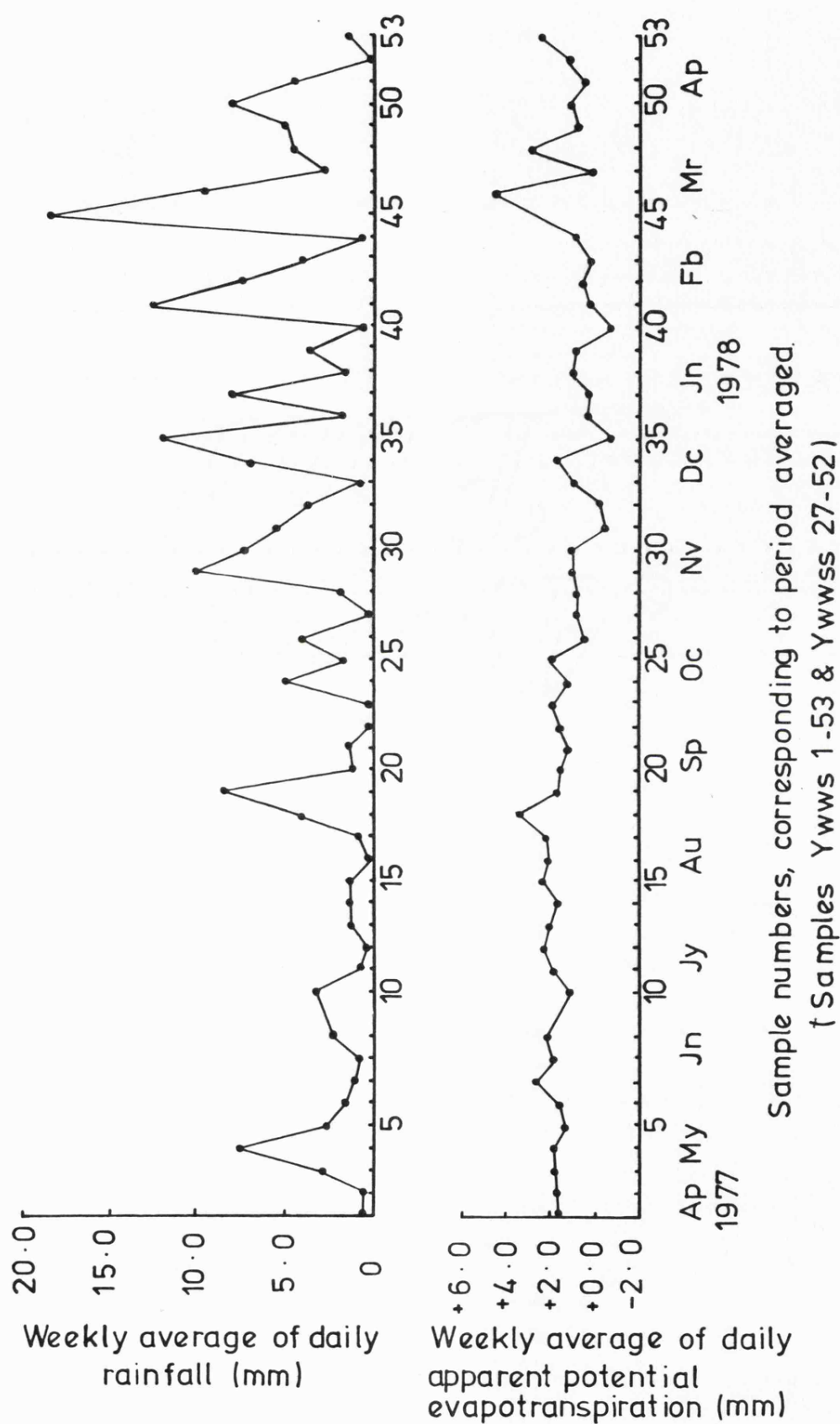


FIG. 7.2. EVAPOTRANSPIRATION & RAINFALL THROUGHOUT APRIL 1977 - 1978. CORRESPONDS TO Ywws 1-53 & Ywwss 27 - 52.

at 95°C, and YWS 1-50 for Sn by the method given by Stanton (1966, p.81).

The results, plotted as raw data, and also smoothed, using a 3-cell rolling mean, are shown in Figures 7.3 to 7.22.

#### 7.2.2. Comparison of seasonal and error variance

The overall seasonal variance was calculated, using a formula similar to that developed in Section 3.2.2.2., (p. 3.5), for each element, except Sn, and this was then compared, via an F test, with the total error variance given for the various elements in Table 3.2 (p. 3.7). The comparisons are summarised in Table 7.1. It will be noted that the seasonal variation is, for most elements, greater than can be accounted for in terms of total error variance alone. The significance of the results for individual elements will be discussed in the appropriate following sub-sections.

#### 7.2.3. Results for individual elements

##### 7.2.3.1. Copper (Figs. 7.3 and 7.14)

Table 7.1 shows that the seasonal variance is significantly greater than the total error variance. Of particular interest in the raw data plot in Fig. 7.3 is the peak shown by samples 25 and 26 corresponding with the heavy rainfall in late September 1976 following the severe summer drought. The three-cell rolling mean plot shows a decline from about 375 ppm in the spring to about 300 ppm throughout the summer and autumn, with the late September high values superimposed upon that trend. Generally higher values were recorded again in the winter, the average being near to 350 ppm. The data for the winter of 1977-78, shown in Fig. 14, appears to confirm that the Cu content of the sediments was generally lower in the summer, when the flow of the river was low, and higher during the more active run-off in the winter.



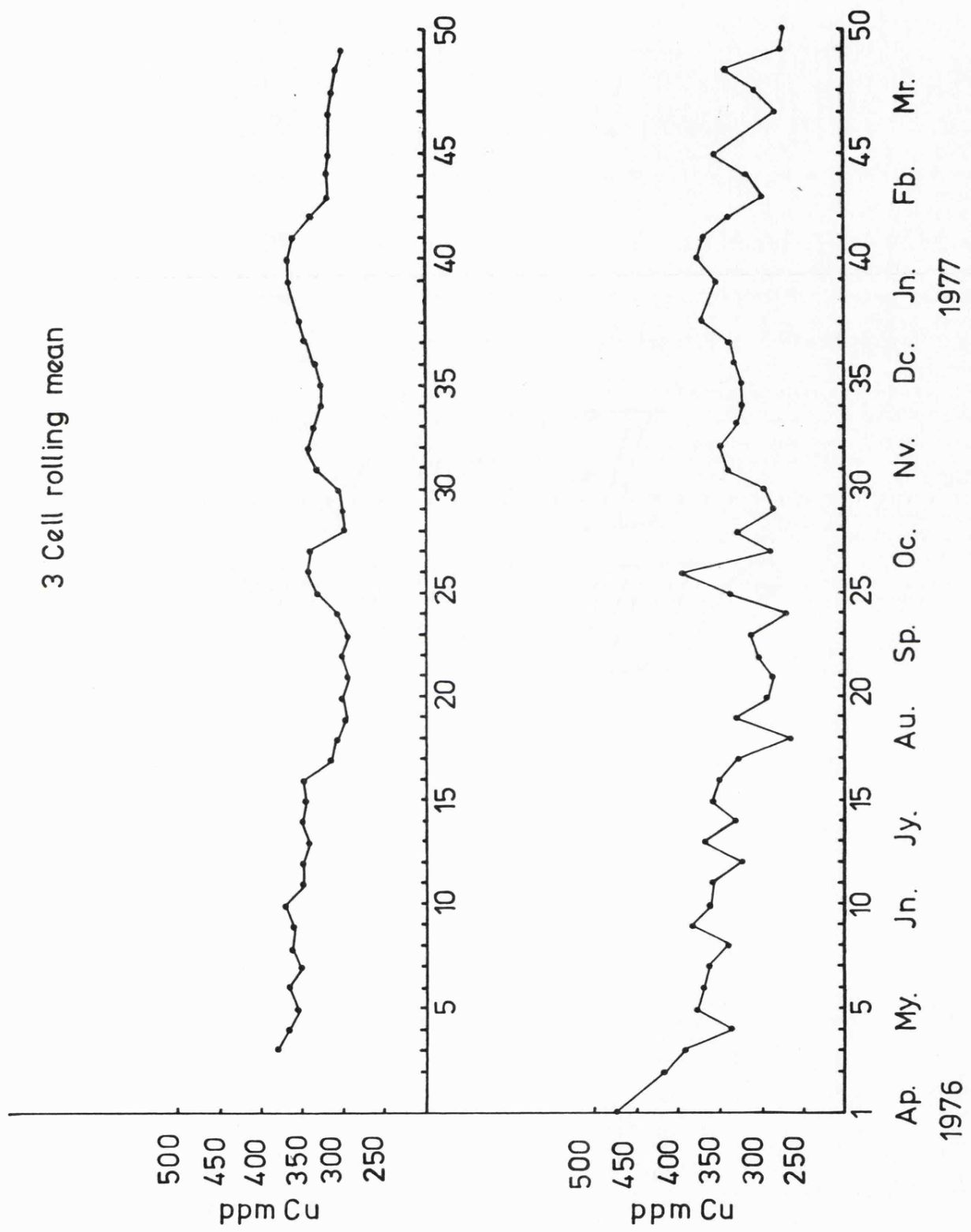


FIG. 7.3 SEASONAL SEDIMENT SAMPLES Yws 1-50. Cu CONTENT

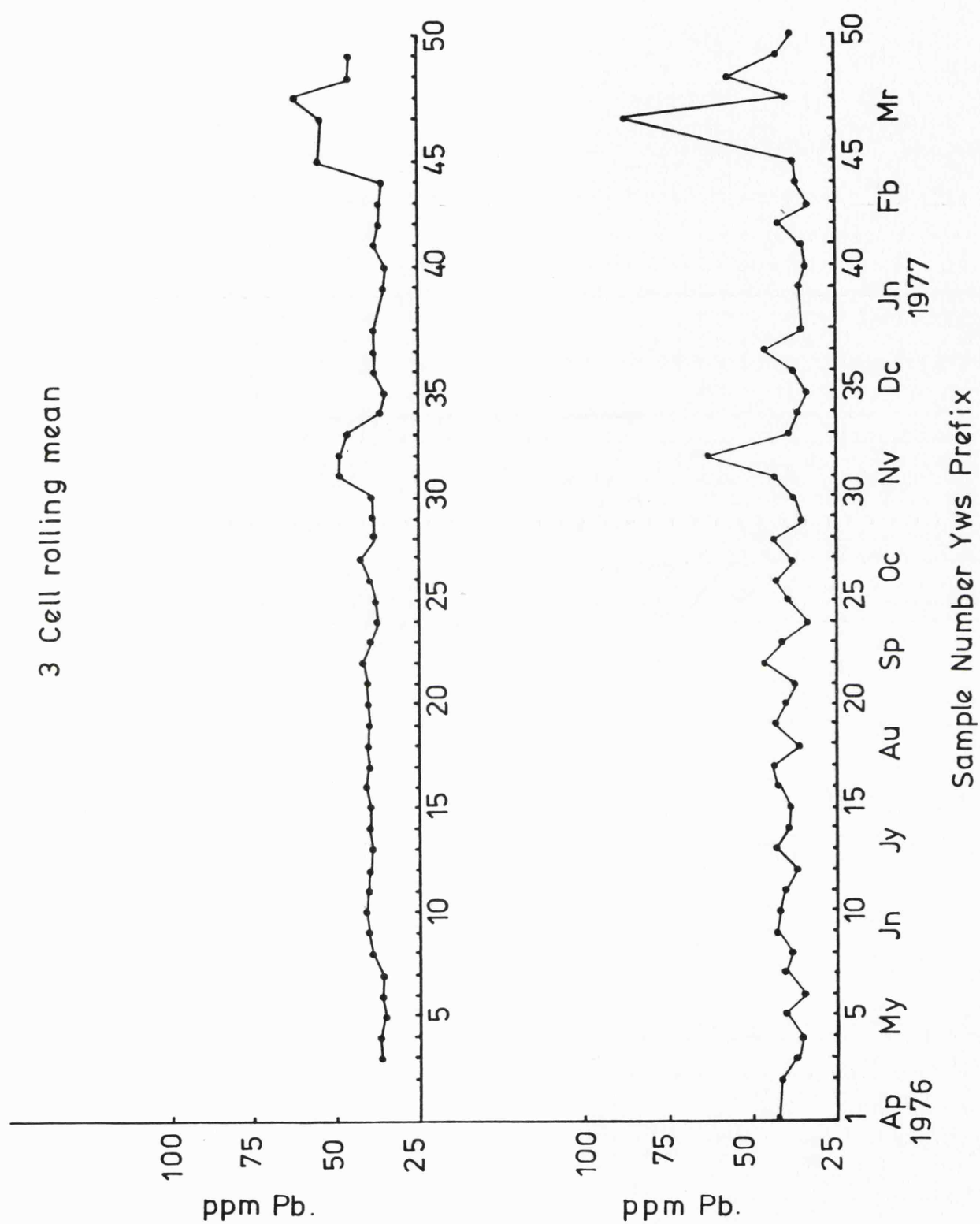


FIG. 7.4      SEASONAL SEDIMENT SAMPLES Yws 1-50. Pb CONTENT.

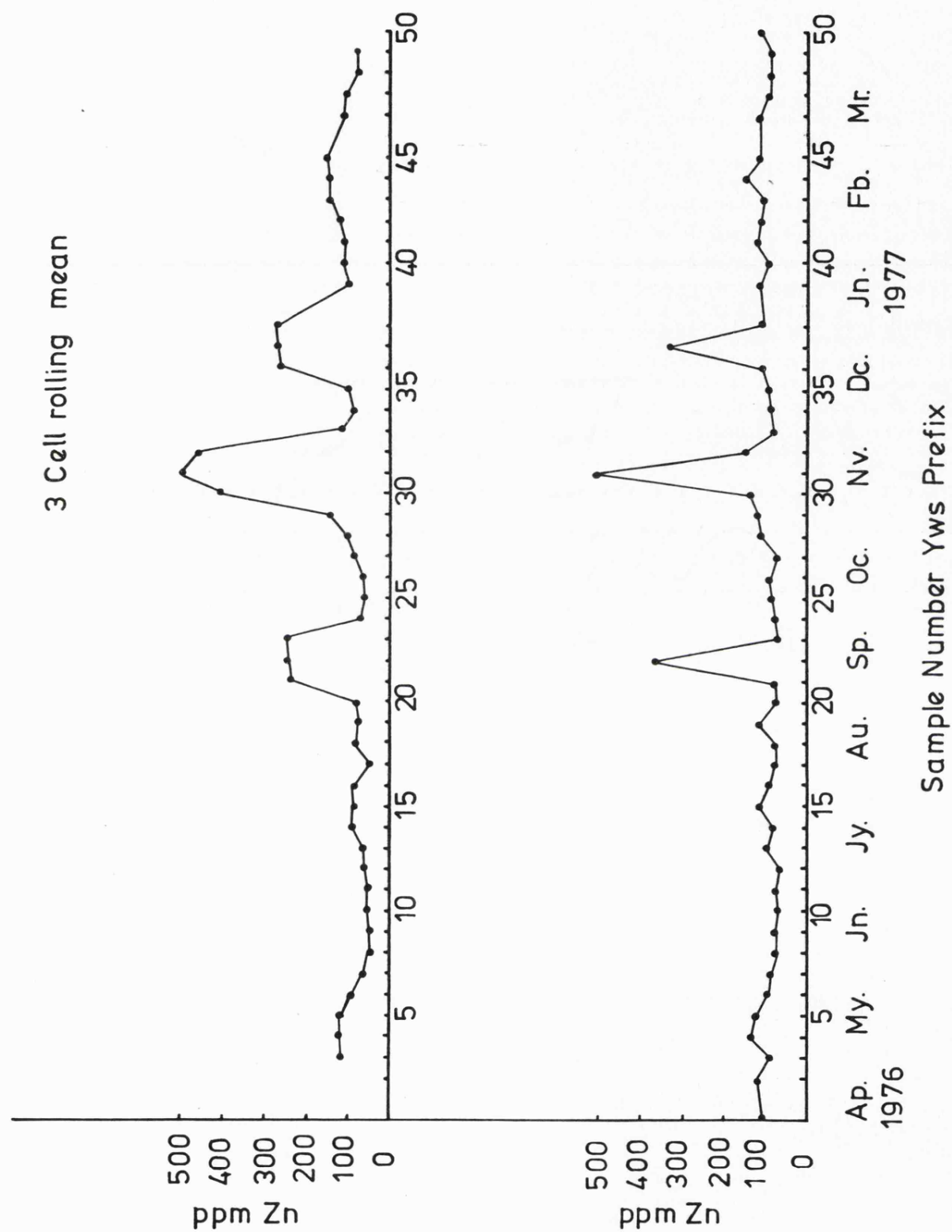


FIG. 7.5 SEASONAL SEDIMENT SAMPLES Yws 1-50. Zn CONTENT

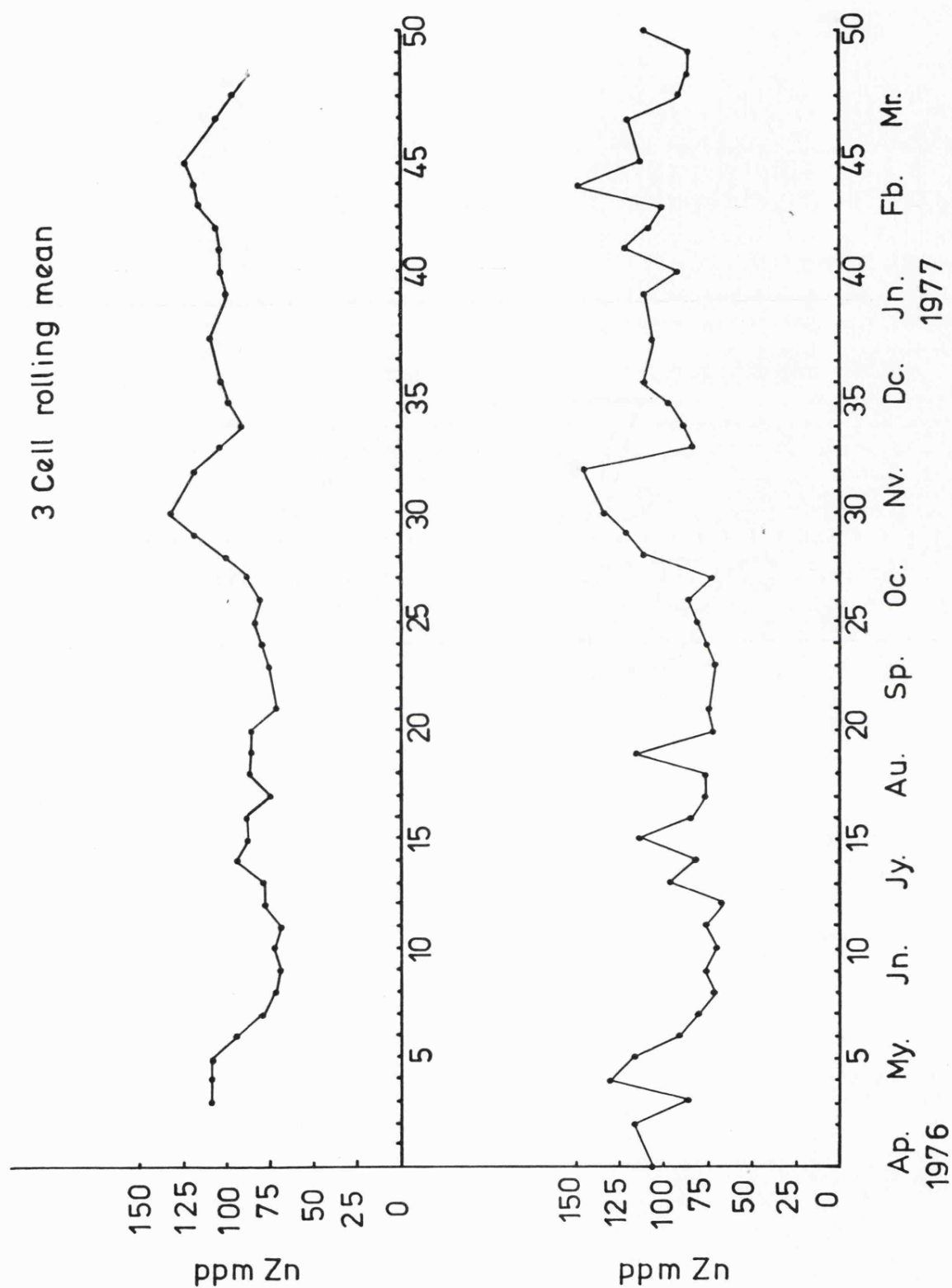


FIG. 7.6 SEASONAL SEDIMENT SAMPLES Yws. 1-50. Zn CONTENT OMITTING HIGH VALUES AT 22, 31 & 37

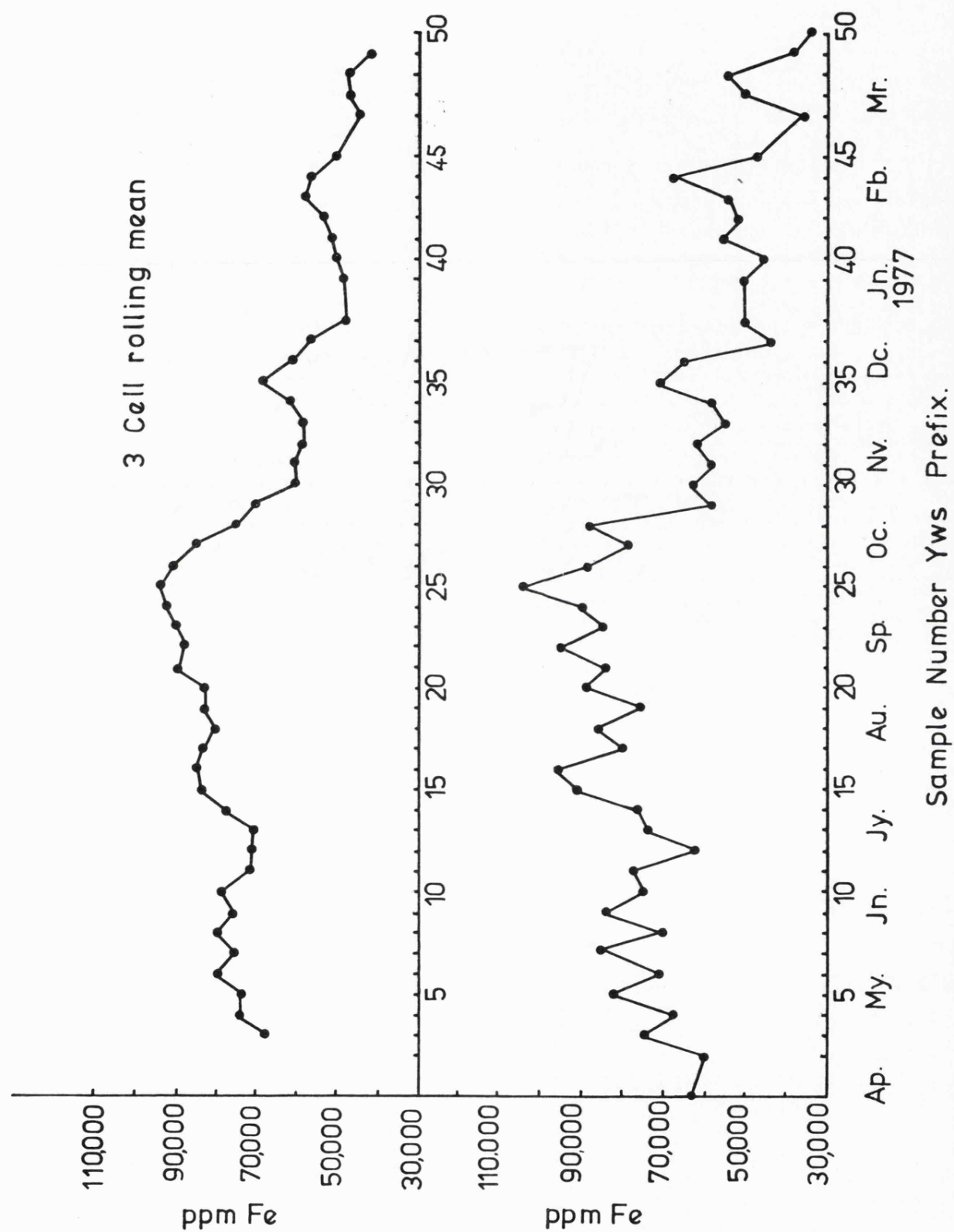


FIG. 7.7 SEASONAL SEDIMENT SAMPLES Yws 1-50.Fe CONTENT.

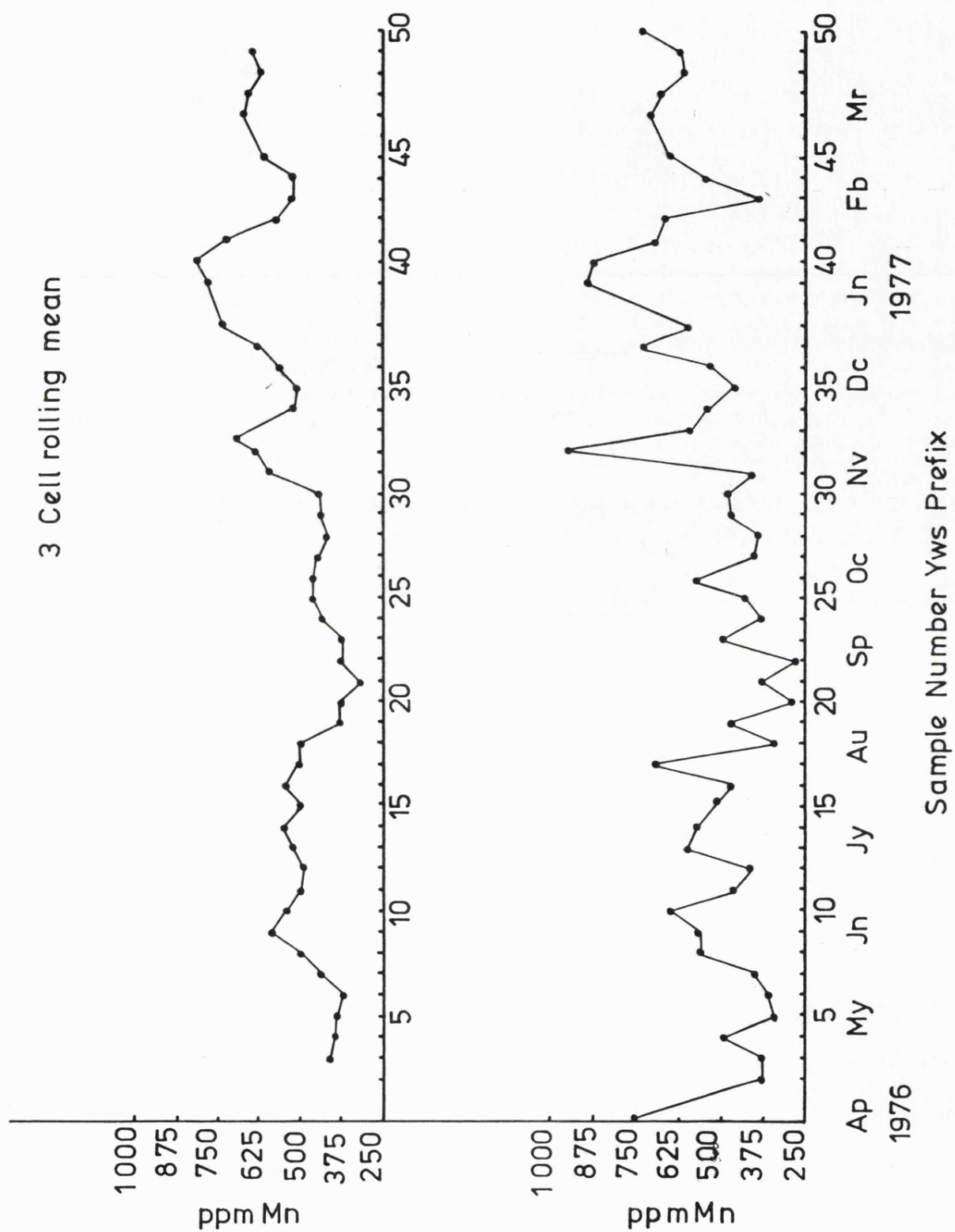


FIG 7-8      SEASONAL SEDIMENT SAMPLES Yws 1-50.Mn CONTENT

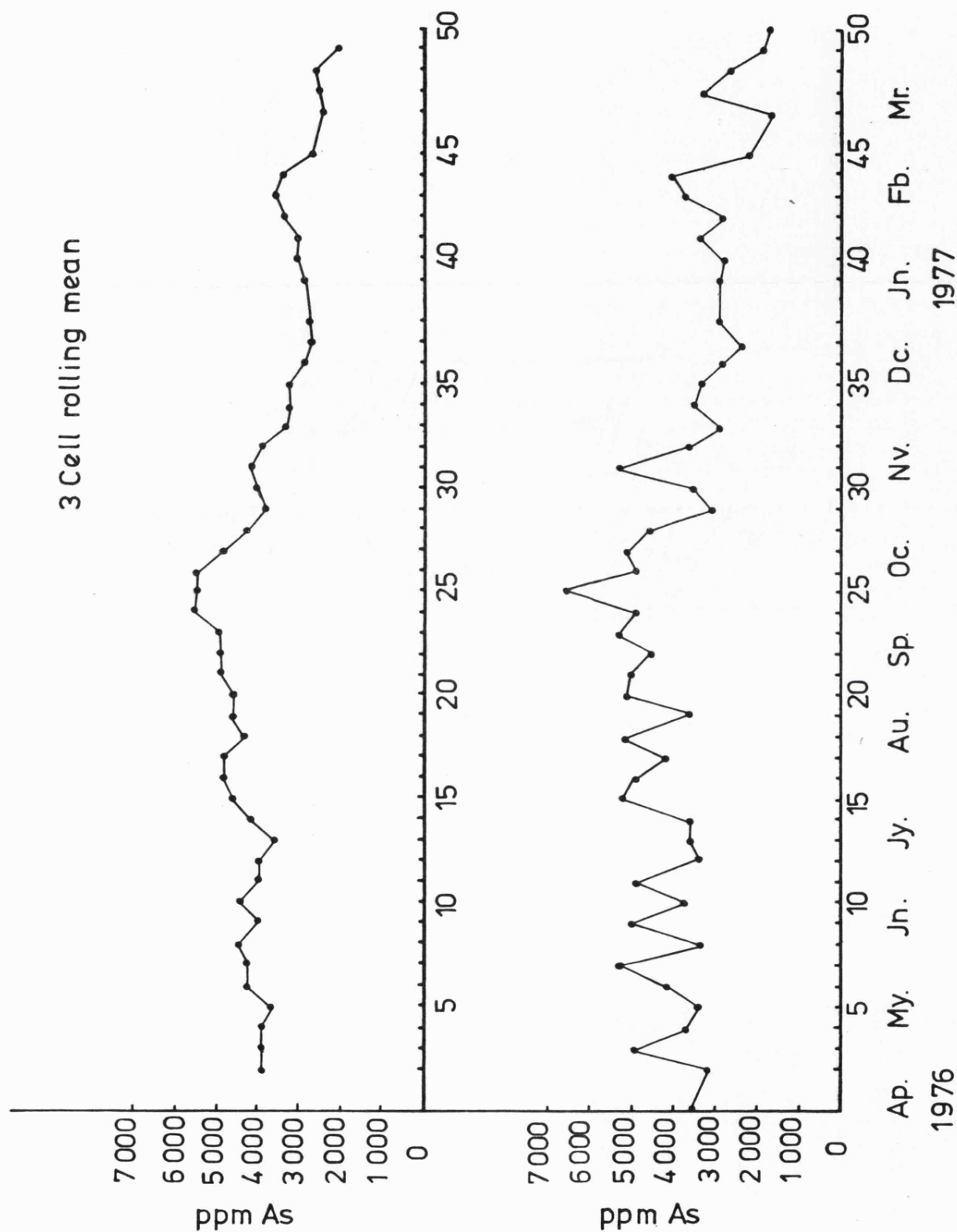


FIG. 7.9 SEASONAL SEDIMENT SAMPLES Yws 1-50. As CONTENT.

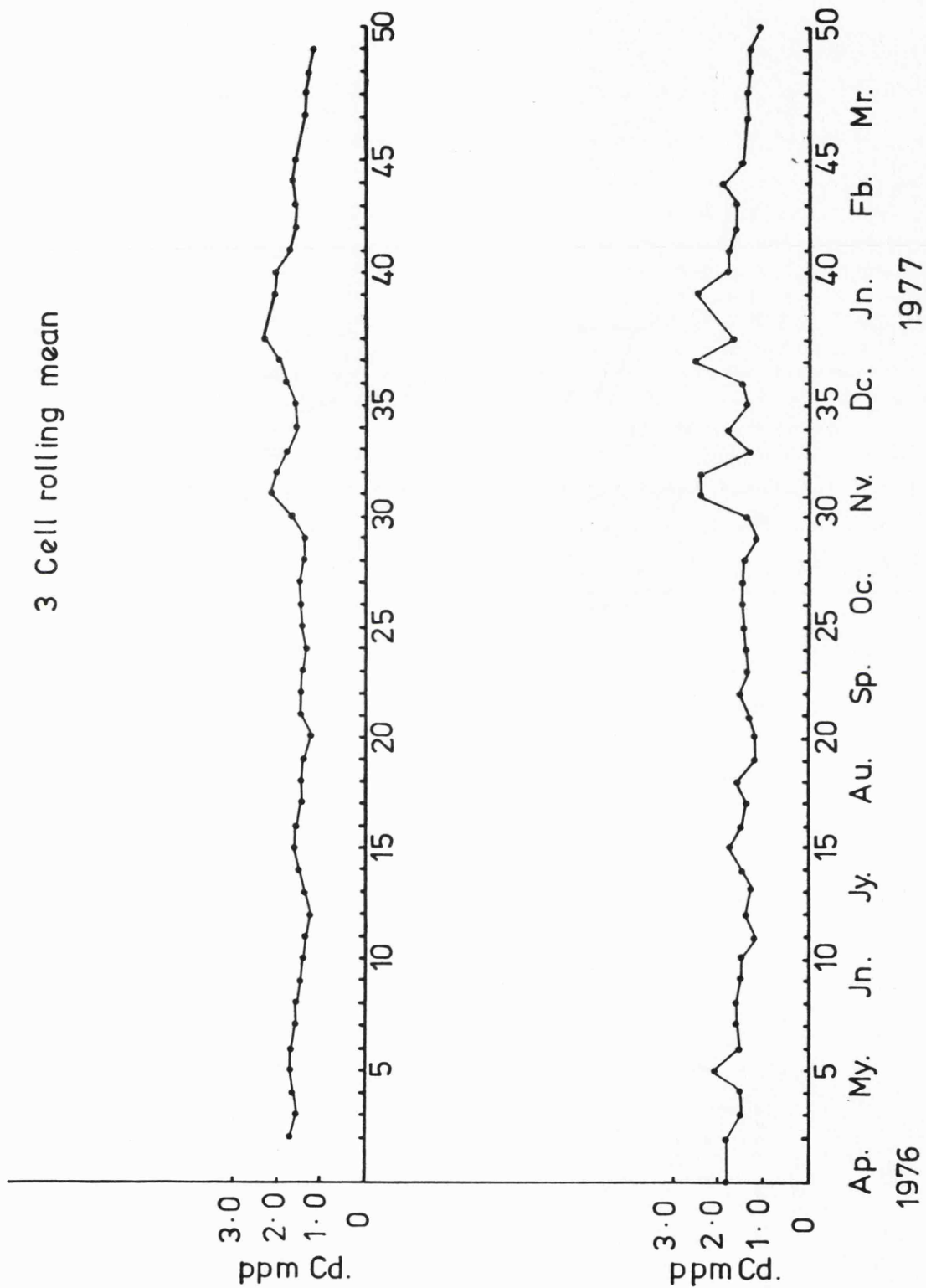


FIG 7.10 SEASONAL SEDIMENT SAMPLES Yws.1 -50.Cd CONTENT.



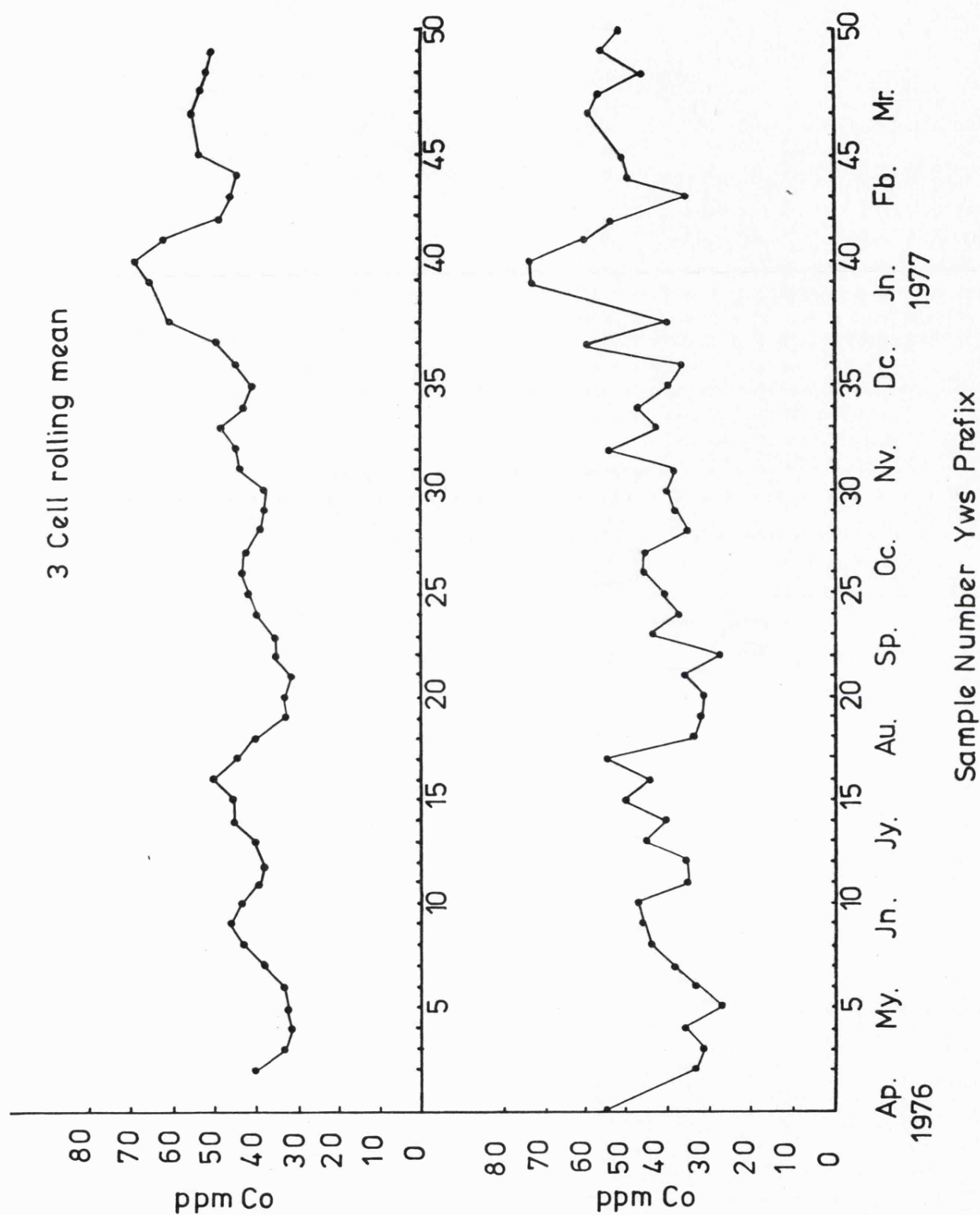


FIG. 7.11 SEASONAL SEDIMENT SAMPLES Yws 1-50. Co CONTENT

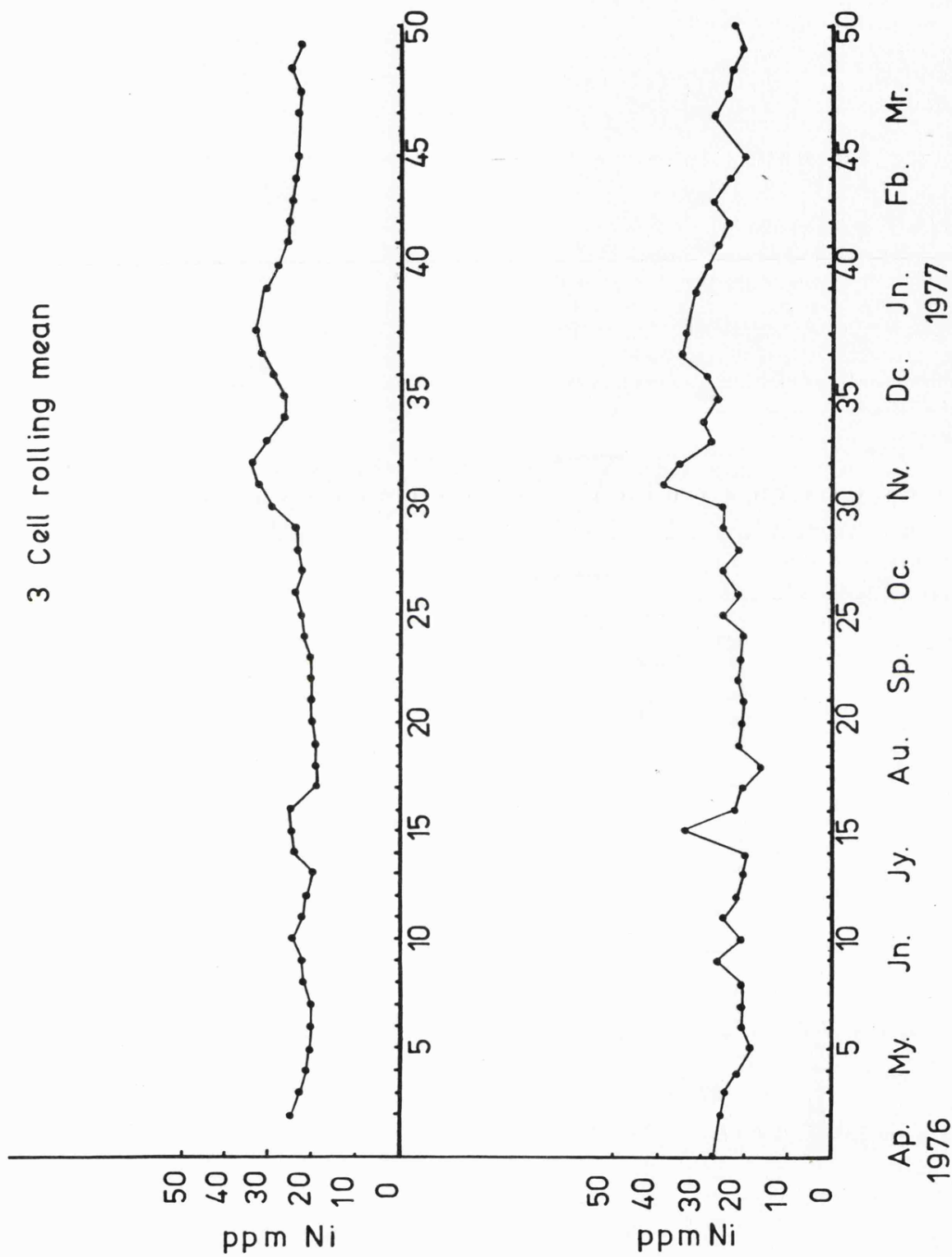


FIG. 7-12 SEASONAL SEDIMENT SAMPLES Yws 1-50. Ni CONTENT

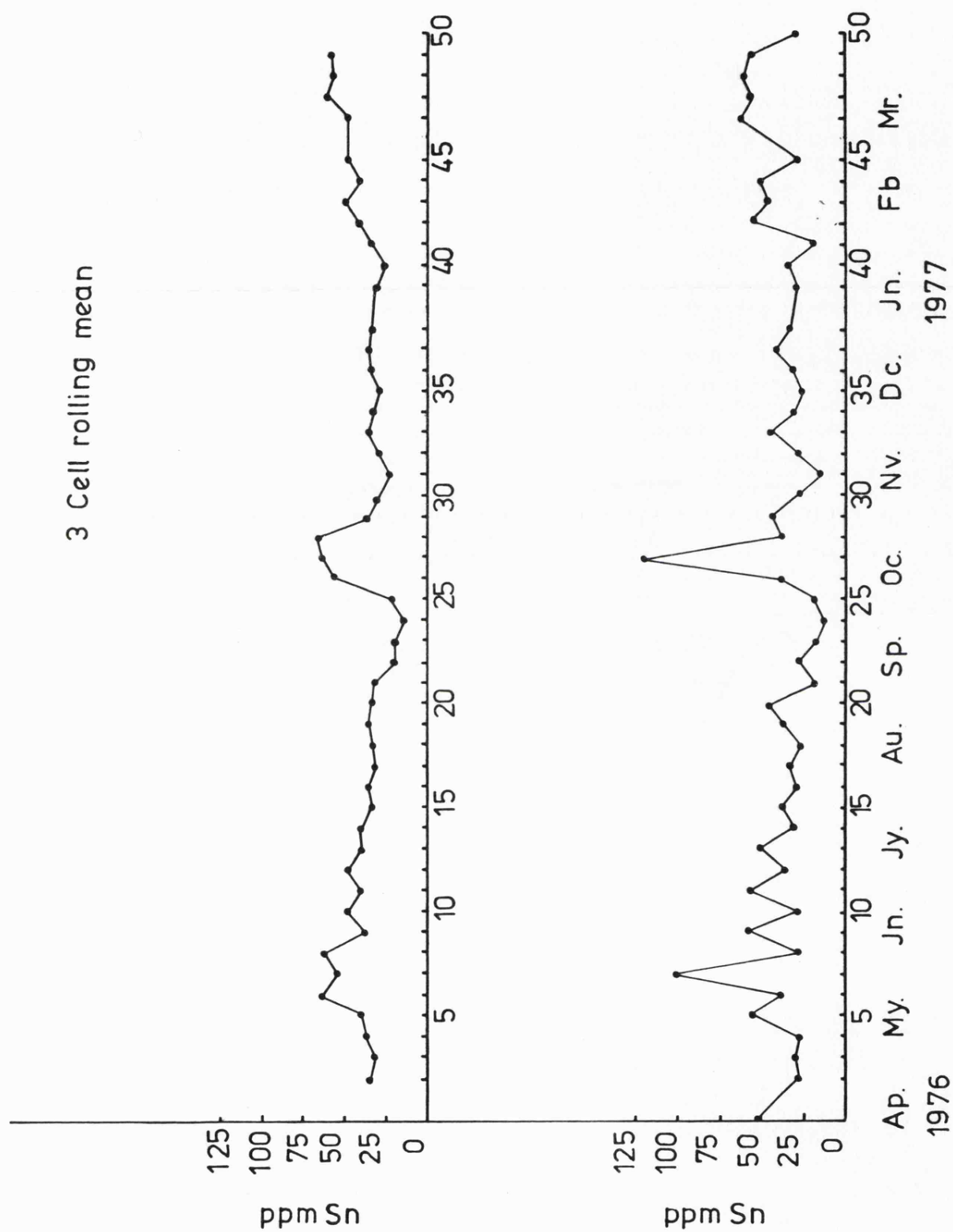


FIG. 7-13 SEASONAL SEDIMENT SAMPLES. Yws 1-50. Sn CONTENT

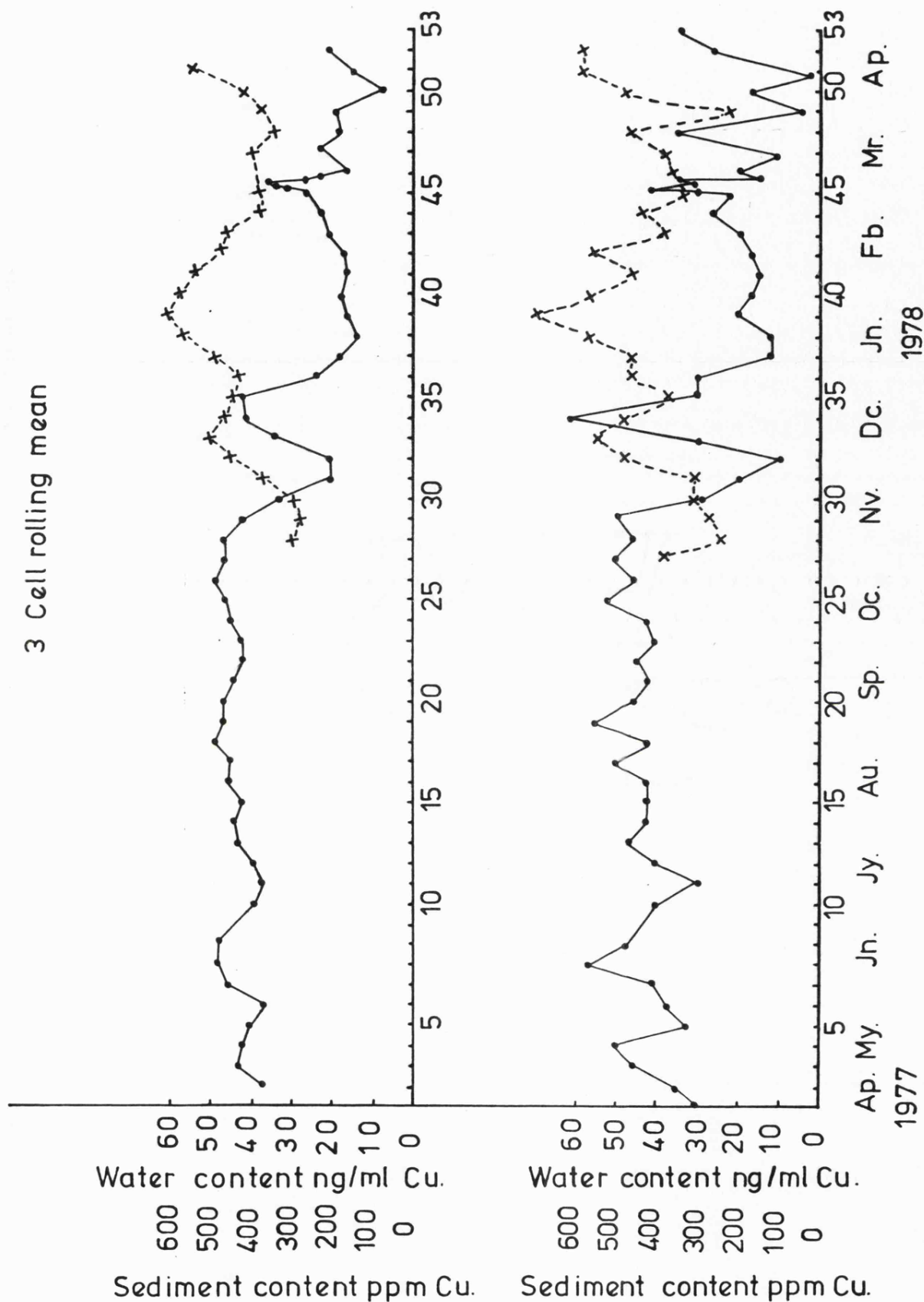
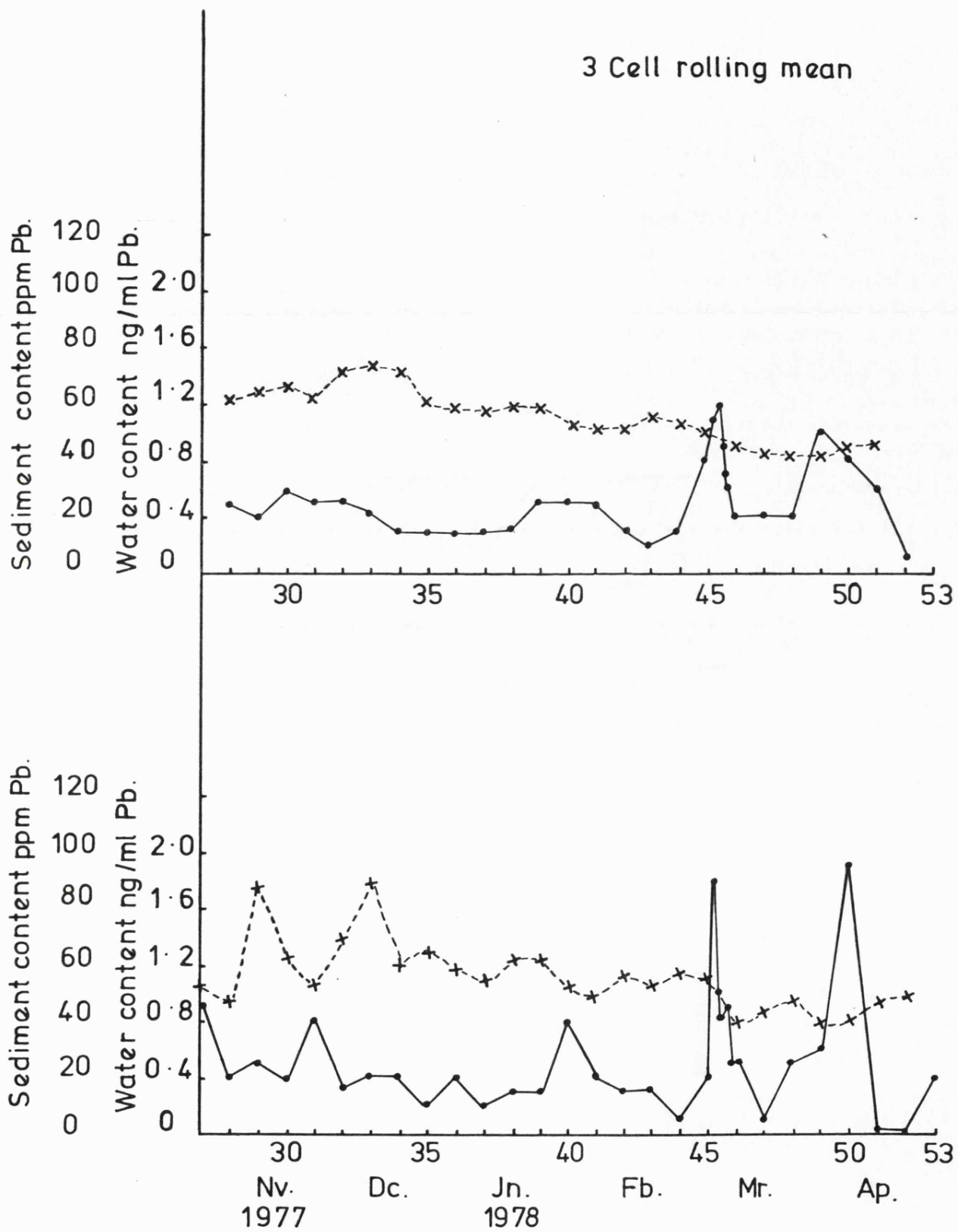


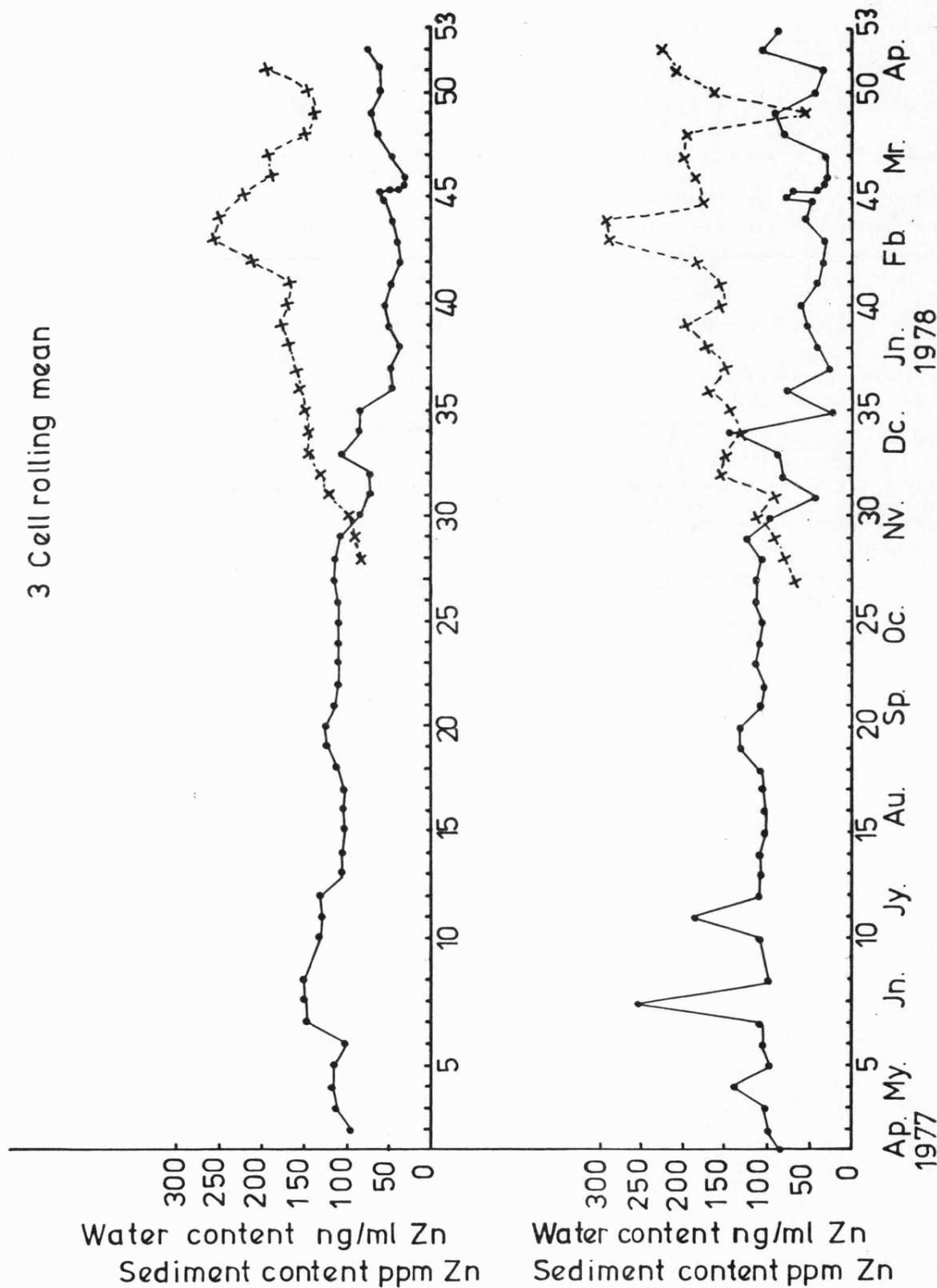
FIG. 7-14 SEASONAL WATER SAMPLES, Ywws 1-53. SEDIMENT SAMPLES, Ywss 27-52. Cu CONTENT.



Sample numbers —•— Water samples, prefix Ywws. x---x Sediment samples prefix Ywss.

**FIG. 7-15** SEASONAL WATER SAMPLES, Ywws 27 - 53. SEDIMENT SAMPLES, Ywss 27 - 52. Pb CONTENT.

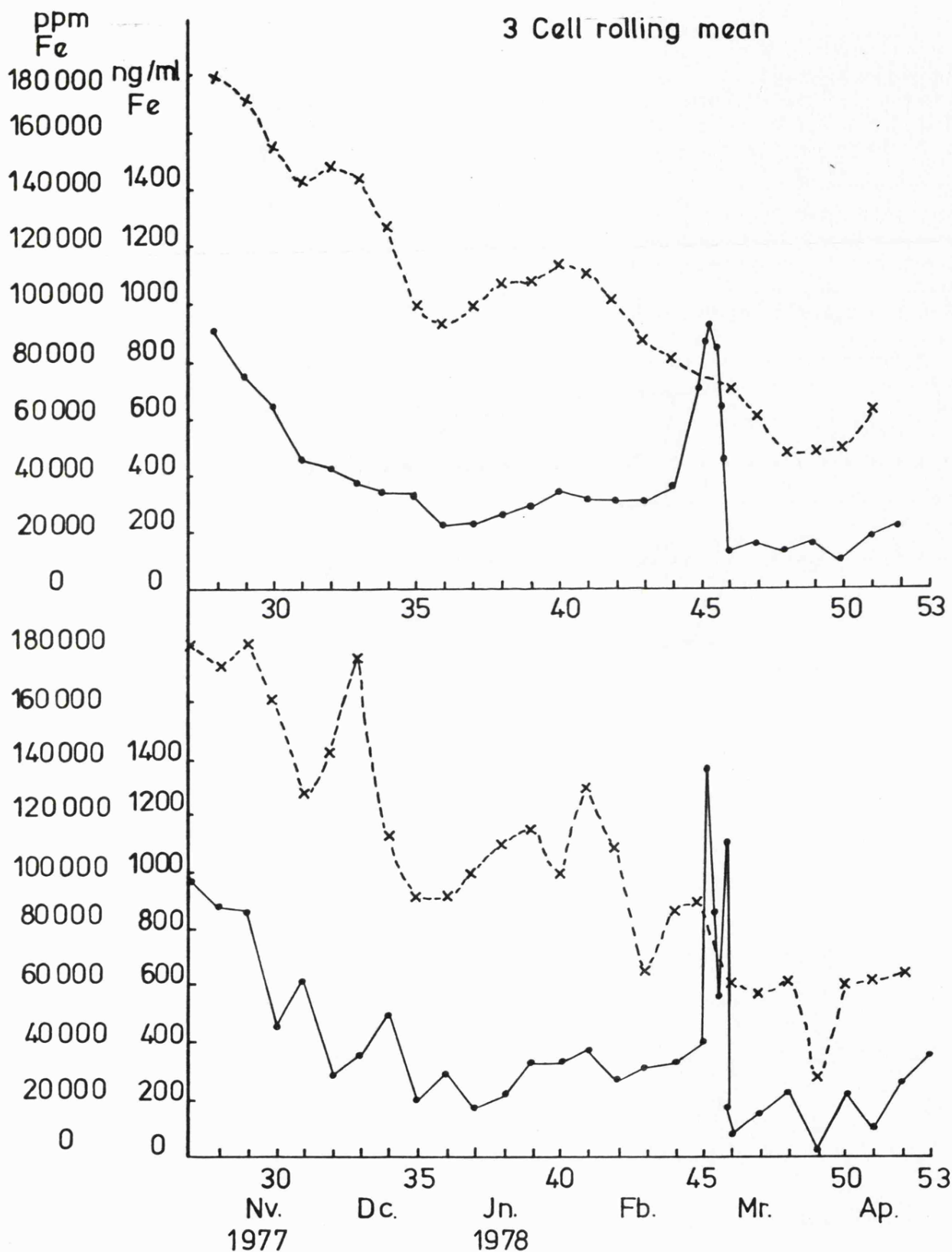
### 3 Cell rolling mean



Sample numbers —•— Water samples, prefix Ywws. x---x Sediment samples, prefix Ywwss.

FIG. 7-16 SEASONAL WATER SAMPLES, Ywws 1 - 53.  
SEDIMENT SAMPLES, Ywwss 27 - 52. Zn CONTENT.





Sample numbers  $\bullet$ — $\bullet$  Water samples, prefix Ywws.  $x$ — $x$  Sediment samples  
Prefix Ywwss.

FIG. 7-17 SEASONAL WATER SAMPLES, Ywws 27 - 53. SEDIMENT SAMPLES, Ywwss 27 - 52. Fe CONTENT.

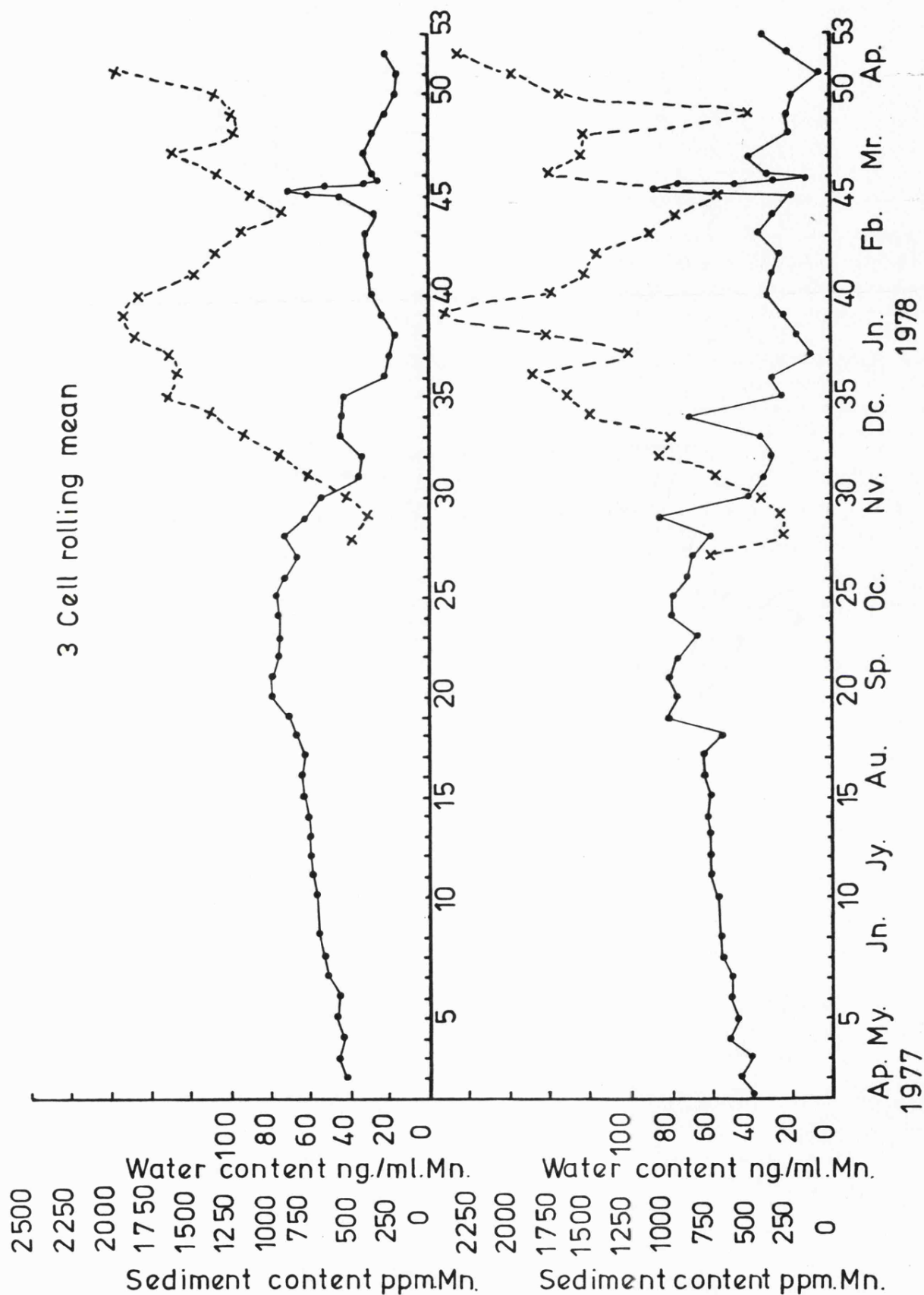


FIG 7-18 SEASONAL WATER SAMPLES, Ywss 1 - 53. SEDIMENT SAMPLES, Ywss 27 - 52. Mn CONTENT.



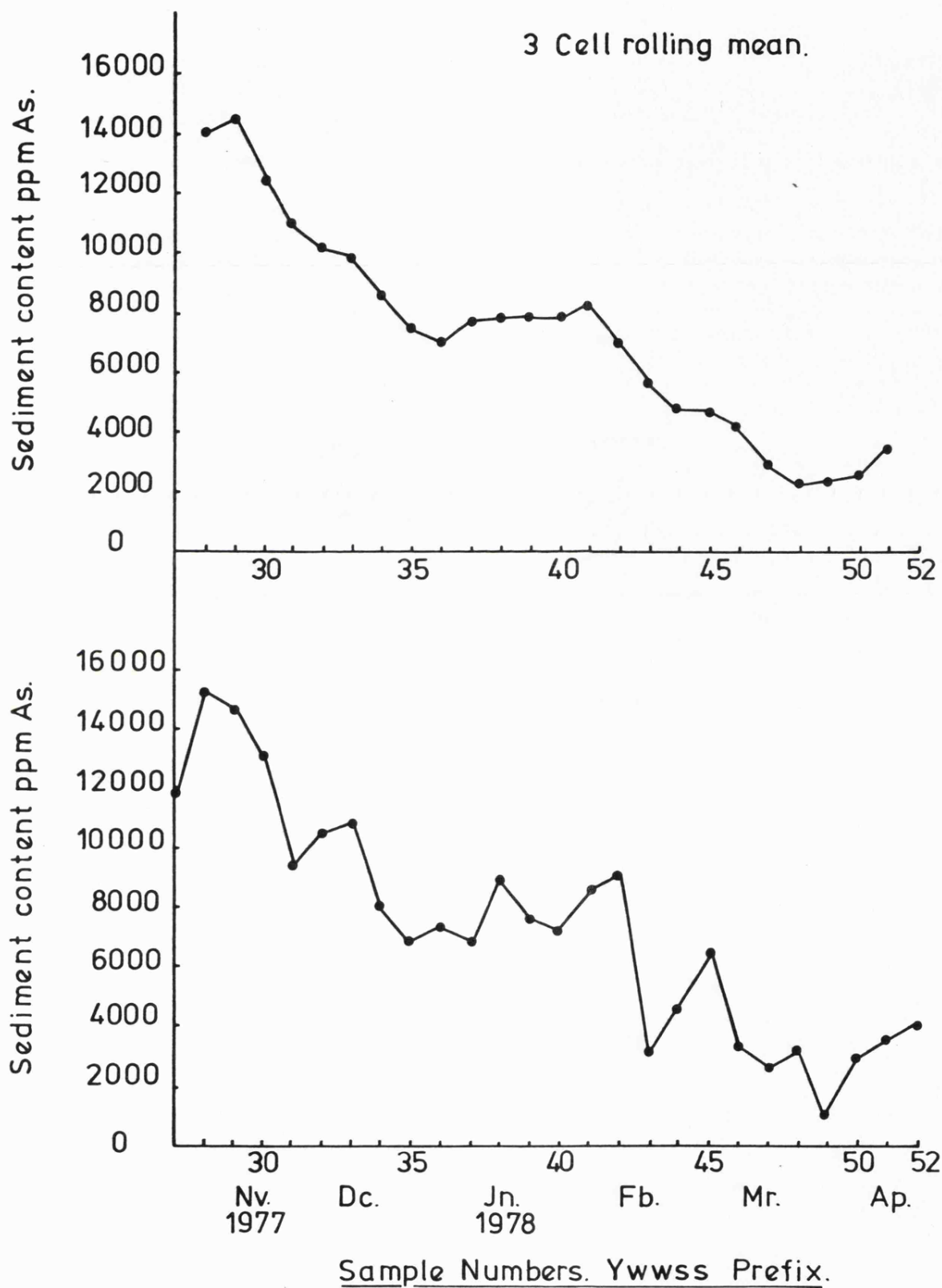


FIG. 7-19 SEASONAL SEDIMENT SAMPLES, Ywwss 27-52. As CONTENT

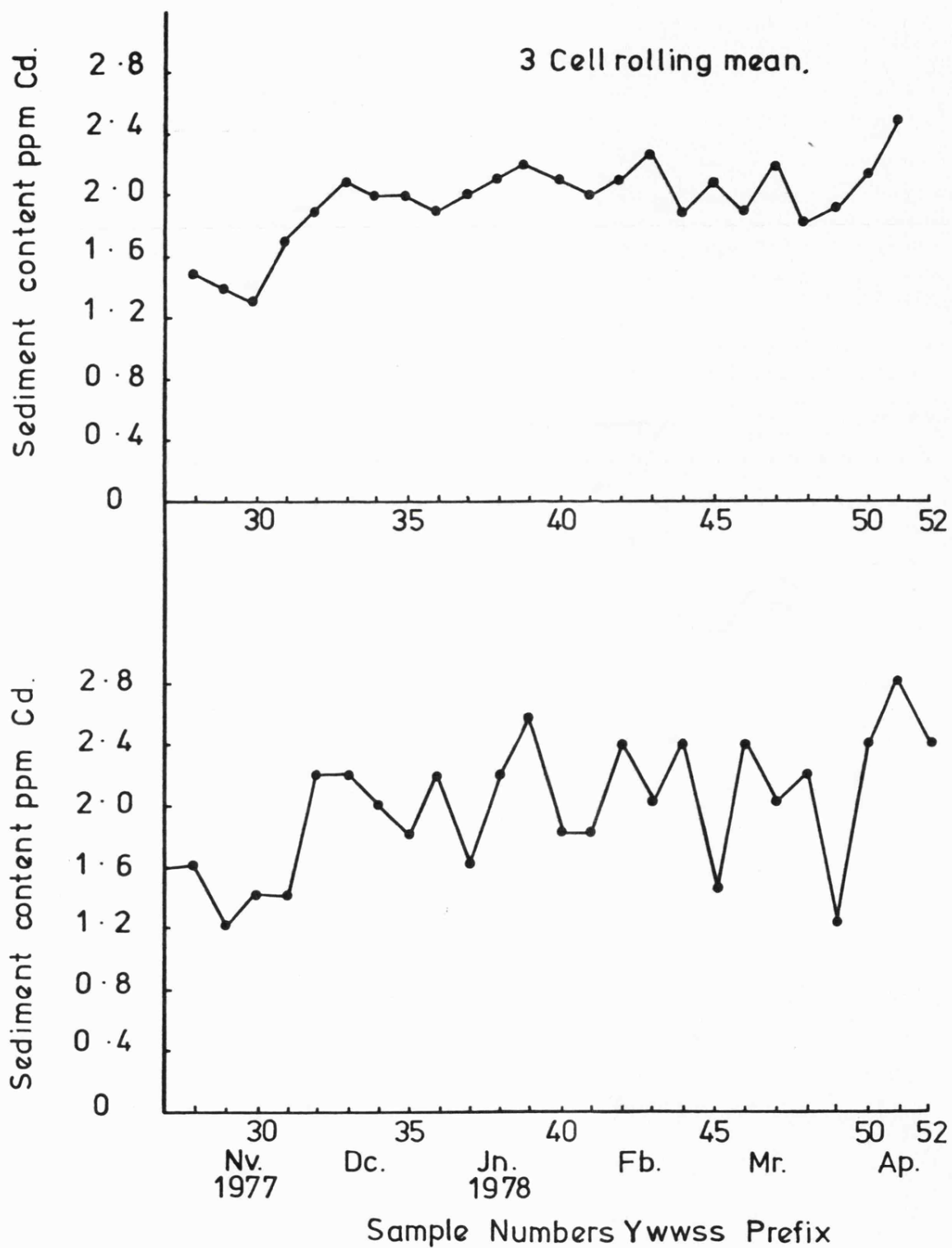


FIG. 7-20 SEASONAL SEDIMENT SAMPLES Ywwss 27-52. Cd CONTENT

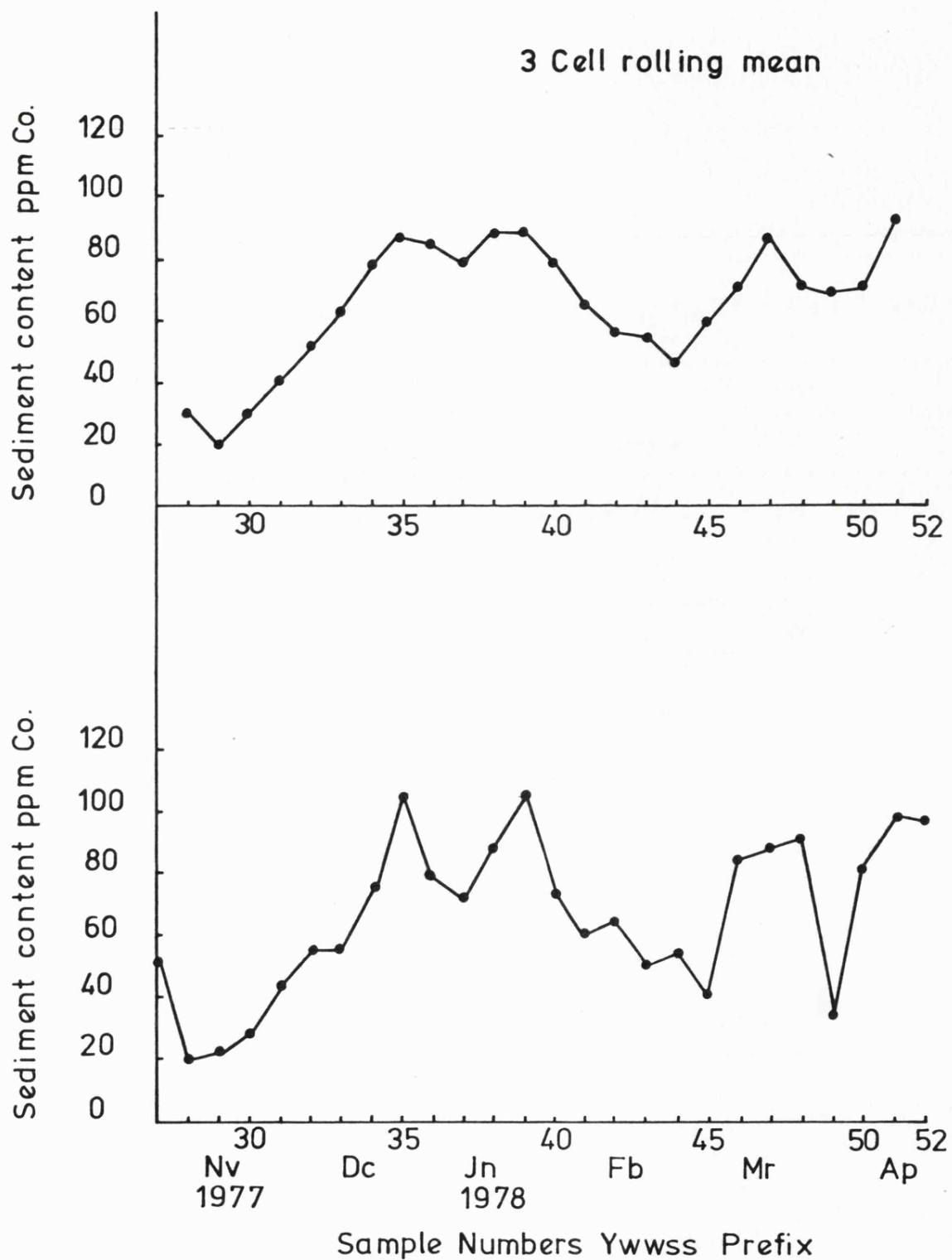


FIG. 7.21 SEASONAL SEDIMENT SAMPLES Ywwss 27-52.Co CONTENT.

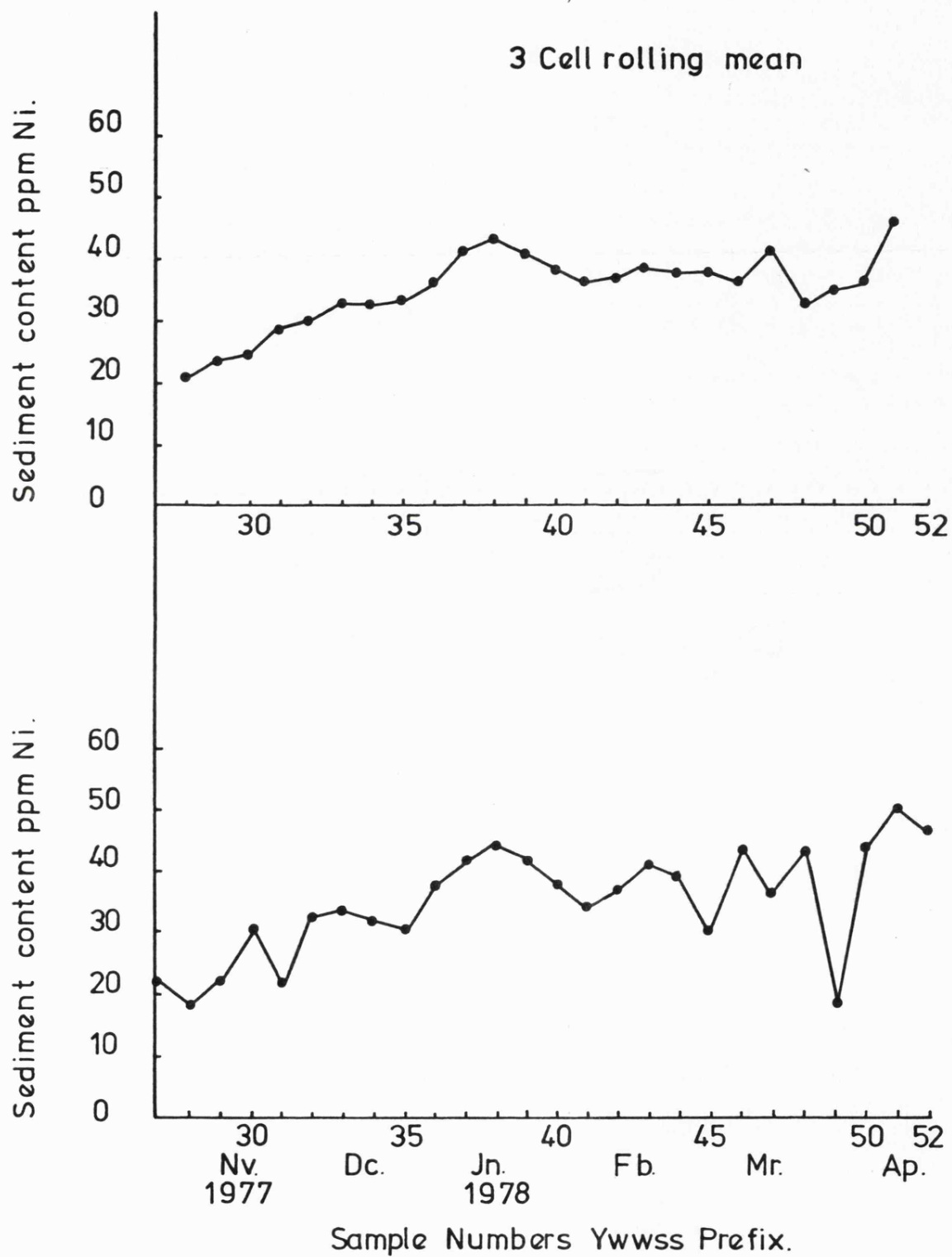


FIG.7-22     SEASONAL SEDIMENT SAMPLES Ywwss 27-52.Ni CONTENT.

**TABLE 7.1** Comparison of seasonal variance and total error variance, via Snedecor's F test, in sediment samples YWS 1 - 50

	$S_{TE}^2$	$S_{SEAS}^2$	F ratio	Result
Cu	1.77	2.89	1.63	SIG**
Pb	1.60	2.44	1.52	NS**
Zn	3.19	3.18	1.00	NS*
Fe	3.64	13.54	3.72	SIG***
Mn	15.00	16.26	1.08	NS*
As	3.89	17.99	4.62	SIG***
Cd	4.21	6.68	1.59	SIG*
Co	4.84	10.47	2.16	SIG***
Ni	3.32	6.77	2.04	SIG***

$S_{TE}^2$  denotes total error variance.

$S_{SEAS}^2$  denotes seasonal variance

SIG denotes difference in variances significant.

NS denotes difference in variances not significant.

\* denotes  $\alpha = 0.10$

\*\* denotes  $\alpha = 0.05$

\*\*\* denotes  $\alpha = 0.01$

All variance values  $\times 10^{-3}$

A marked positive correlation was noted between the Cu content of the sediment, and the abrupt rainfall increase at the end of the long summer drought of 1976.

#### 7.2.3.2. Lead (Figs. 7.4 & 7.15)

In calculating the seasonal variance, if the high values for samples 32 and 46 are omitted, the difference between seasonal and total error variance is not significant.

There were no apparent climatic reasons for the high values in samples 32 and 46, nor is there any record of human activities in the Reserve which might account for them. The 3-cell rolling mean plot in Fig. 7.4 shows no seasonal variation, other than the peaks caused by samples 32 and 46, and it is therefore concluded that the Pb content of the sediments was largely unaffected by seasonal fluctuations.

#### 7.2.3.3. Zinc (Figs. 7.5, 7.6 & 7.16)

Table 7.1 demonstrates that the seasonal and total error variances are indistinguishable even at the 90% confidence level.

Figure 7.5 shows, in the raw data, that three very high values punctuated the general level of about 100 ppm. Sample 22 was the first sample collected after a 5 week long completely dry spell (see Fig. 7.1), but there were no obvious reasons for the other two high values in samples 31 and 37. In order to evaluate seasonal variations, these three high values were omitted and the data re-plotted as Fig. 7.6. From the 3-cell rolling mean plot, it can be seen that the winter level of about 110 ppm was replaced by a slightly lower level of about 80 ppm in the summer period. The same trend can be seen in the 3-cell rolling mean plot in Fig. 7.16, with a winter level of 150 ppm or so, rising from a summer level which appears to be about 80 ppm.

The fact that variation was observed for Zn, and that it corresponds with climatic factors, as well as paralleling the Cu results, implies that the Zn seasonal variation is significant, despite it being not significantly greater than the total error variance.

#### 7.2.3.4. Iron (Figs. 7.7 & 7.17)

The difference between seasonal and total error variance is shown by Table 7.1 to be significant, even at the 99% confidence level.

Figure 7.7 demonstrates that the Fe content of the sediments YWS 1 - 50 showed a pronounced seasonal fluctuation, with high values, averaging about 80,000 ppm, in the summer months and much lower values, averaging about 50,000 ppm, in the winter. The fall from high to low values happened quite rapidly over the period from late September to early November. The same trend is apparent in the YWWSS 27 - 52 samples, shown in Fig. 7.17, and in this case the variation was even more pronounced, falling from 180,000 ppm Fe in late October to an average mid-winter figure of about 80,000 ppm.

#### 7.2.3.5. Manganese (Figs. 7.8 & 7.18)

The difference between seasonal and total error variance, shown compared in Table 7.1, is not significant, even at the 90% confidence level.

The 3-cell rolling mean plot in Fig. 7.8 does show a generally low level in the late summer and early autumn around 400 ppm, and generally higher, though somewhat erratic values in the winter, averaging about 600 ppm. A similar trend may be observed in Fig. 7.18, although a feature of this plot is the considerable fluctuation in values during early 1978, which ranged between 500 and 2300 ppm.

## 7.3.2.6. Arsenic (Figs. 7.9 &amp; 7.19)

Table 7.1 demonstrates that seasonal variation is significantly larger than total error variance.

Fig. 7.9 shows that for the YWS 1 - 50 samples, the summer level for As was about 5000 ppm, and that an average level of about 3000 ppm was recorded in the samples collected during the winter. Fig. 7.19 shows that a similar trend, from high summer values to low winter ones, may be observed for the YWWS 27 - 52 samples, although the higher levels, 1400 ppm in the autumn, reflect the fact that the latter samples were collected in Yarner Stream above the Woodcock Stream tributary. The similarity between the As and Fe results is not surprising in view of the discussion presented in Section 5.3.3. (p. 5.41).

## 7.3.2.7. Cadmium (Figs. 7.10 &amp; 7.20)

Table 7.1 demonstrates that the total error variance is smaller than the seasonal variation, but only at the 90% confidence level.

Figure 7.10 demonstrates that through the spring and summer of 1976, the Cd content of the sediments remained constant at about 1.5 ppm. Slightly higher and more erratic values were recorded between late October and early February, resulting in the 3-cell rolling mean having an average of about 2.0 ppm during that period. A similar trend appears to be discernable from the results in Fig. 7.20.

## 7.3.2.8. Cobalt (Figs. 7.11 &amp; 7.21)

Table 7.1 shows that the total error variance is significantly less than the seasonal variance, even at the 99% confidence level.

The Co results shown in the raw data plot of Fig. 7.11 were somewhat erratic, and the 3-cell rolling mean plot is very little clearer. There appeared to be a minimum during the late summer, in the region of 35 ppm, with a maximum in December and January, the mean winter



content being about 50 ppm. This trend is tentatively confirmed by Figure 7.21 for the YWSS 27 - 52 samples, but the highly erratic nature of the values makes interpretation doubtful.

#### 7.3.2.9. Nickel (Figs. 7.12 & 7.22)

Table 7.1 demonstrates that the difference between total error and seasonal variances is significant, even at the 99% confidence level.

The results, shown in the 3-cell rolling mean plot of Fig. 7.12, indicate a minimum Ni content in the sediments collected in late spring, summer and early autumn, averaging about 20 ppm. The winter level, which averaged about 30 ppm, declined during February towards the summer level. A very similar pattern is revealed by the results from samples 27 - 52 shown in Fig. 7.22, although no spring decline towards lower levels is apparent in this plot.

#### 7.2.3.10 Tin

Samples YWS 1 - 50 were analysed for Sn and the results, shown in Fig. 7.13, indicate that low concentrations of Sn were present, except for two erratic high values, samples 7 and 27. Sample 27 corresponds to the rainfall maximum in early October, when the weekly average of daily rainfall exceeded 18 mm (see Fig. 7.1). The results displayed by the 3-cell rolling mean plot, went to a minimum of about 20 ppm during the summer drought, and rose in September and October to about 40 ppm as the sediment load of the river was increased by more rapid run-off.

### 7.3 WATER SAMPLES

#### 7.3.1. Introduction

Water samples were collected at YW 10 in Yarner Stream, at weekly intervals, from mid-April 1977 to mid-April 1978. The flood waters, which followed heavy snowfall in late February 1978, were sampled at daily intervals. Following the analysis of samples described in Section 6.3.2. (p. 6.9 ), it was initially felt that acidification was unnecessary and so samples YWWS 1 - 25 were not acidified on collection. Subsequently, when the results from Section 6.3.3. (p.6.12) became available, the advisability of acidifying water samples was appreciated, especially if analysis is to be carried out for Fe. Thus, samples YWS 26 - 53 were acidified on collection with 0.1 ml of ultra pure hydrochloric acid. A sample, YWW 10, was collected at locality 10 on 4.4.77, and analysed numerous times (see Section 6.3.3., p. 6.12). The results are shown in Tables 6.6, 6.7, 6.8 and 6.9 for Mn, Fe, Zn and Cu respectively. It is apparent that the Fe results from the unacidified sample are meaningless, but that the Cu, Zn and Mn content of water from this locality is substantially unaffected by delays prior to analysis. Therefore, all water samples were analysed for Cu, Zn and Mn, but only the acidified samples, YWWS 26 - 53 were analysed for Fe.

Detection of Pb was only possible after the acquisition, in December 1977, of a graphite furnace atomisation unit for the AAS. Since no results concerning the behaviour of Pb in solution with respect to time were available, analysis for Pb was confined to the acidified samples.

A rapid thaw followed the heavy snowfall of mid-February 1978, and five extra samples were collected between samples YWWS 45 and 46 to examine the effects of the flooding on metal content in solution.

### 7.3.2. Comparison of seasonal and error variance

Total error variance was calculated for Cu, Zn, Fe and Mn in Section 6.2.3. (p. 6.6 ), and the values are shown in Table 6.3. Table 7.2 shows these values compared with the seasonal variance values, calculated from the YWWS samples. It can be seen that, at the 95% confidence level, the seasonal variance is greater than the total error variance for the four elements under consideration

TABLE 7.2 Comparison of seasonal variance and total error variance, via Snedecor's F test, in water samples YWWS 1 - 53

	$S_{TE}^2$	$S_{SEAS}^2$	F ratio	Result
Cu	0.46	85.81	186.5	SIG***
Zn	35.90	60.34	1.68	SIG**
Fe	7.65	175.9	23.0	SIG***
Mn	8.51	62.92	7.4	SIG***

$S_{TE}^2$  denotes total error variance.

$S_{SEAS}^2$  denotes seasonal variance

SIG denotes difference in variances significant.

NS denotes difference in variances not significant.

\* denotes  $\alpha = 0.10$

\*\* denotes  $\alpha = 0.05$

\*\*\* denotes  $\alpha = 0.01$

All variance values  $\times 10^{-3}$ .

### 7.3.3. Results for individual elements

#### 7.3.3.1. Copper

The Cu analyses of samples YWWS 1- 53 are shown in Fig. 7.14.

A prominent feature of these results is the fairly rapid change from the late spring and summer values, approximately 40 ng/ml, to the lower, rather erratic winter values, which averaged about 20 ng/ml. In addition, the samples collected between mid-July and mid-October show the least rapid fluctuation.

The run-off during the flood period, (between samples 45 and 46) showed a peak in metal content which would not have been observed had only the two weekly samples, 45 and 46, been collected.

The stream was also in flood on the day when sample 34 was collected, as over 40 mm of rain had fallen in the previous 72 hours. The rainfall data in Fig. 7.2 does not demonstrate this fact very clearly, because of the weekly averaging technique adopted.

#### 7.3.3.2. Lead.

The results of analysis of samples YWWS 27 - 53 for Pb are shown in Fig. 7.15. A peak, above the general background level of 0.4 ng/ml, corresponded to the floods (samples 45 and 46) and another peak occurred in late March, when sample 50 was collected, at a time when the stream was also in spate, there having been in excess of 32mm rain in the 48 hours prior to the sample collection. Apart from these peaks, the changing seasons did not appear to have a marked effect upon the Pb content of the water.

#### 7.3.3.3. Zinc.

The results of analysis of samples YWWS 1 - 53 for Zn are shown in Fig. 7.16. The 3-cell rolling mean plot shows a pronounced winter minimum in Zn content, when average metal values fell to about 50 ng/ml. During the spring, summer and early autumn the average was about 120 ng/ml.

The results for the period from July to October, when rainfall was generally light, showed very little fluctuation, whereas throughout the winter the results tended to be much more erratic.

A subdued peak in values marked the period of flooding in late February, and sample 34, again collected when the stream was in spate, was also high. No obvious climatic feature can be found to account for the peaks in late June and late July, (samples 8 and 11) nor is there any record of human activities within the Reserve which might account for these high values.

#### 7.3.3.4. Iron.

The analyses of samples YWWS 27 - 53 for Fe are shown in Fig. 7.17 and demonstrate that the Fe content of the Yarner Stream experienced a steady decline from about 900 ng/ml in late October, to a minimum of about 200 ng/ml in March. Upon this general trend was superimposed a sharp peak which corresponded with the samples collected during the floods in late February.

#### 7.3.3.5. Manganese.

The analytical results for Mn from samples YWWS 1 - 53 are shown in Fig. 7.18, and demonstrate that a fairly smooth seasonal fluctuation in soluble Mn was detected during the period under investigation.

From the late spring value of about 40 ng/ml the metal content rose smoothly to a late summer - early autumn maximum of about 80 ng/ml and then fell sharply during October to reach a winter level of about 30 ng/ml. A sharp peak in values was associated with the floods in late February, and sample 34 was also found to be high in Mn, as it was for Cu and Zn. Successive samples exhibited more erratic metal contents in the winter than in the summer.

#### 7.4 INTERPRETATION OF RESULTS

It was shown in sections 7.2.2 and 7.3.2 that for the majority of elements, both seasonal sediment sample variance and seasonal water sample variance, for the periods under consideration, were greater than total error variance. The difference between seasonal and total error variance for the Pb content of the sediments was not significant and the Pb values do not show variations with any systematic seasonal trend to them. Differences between seasonal and total error variance for Zn and Mn contents of the sediments were also found to be non-significant, but, in the case of both these elements, patterns which can be related to the changing seasons, were observed. These patterns parallel the variations observed for other elements where the differences in variances were found to be significant, and, on the strength of this, they will be included in the following discussion.

The overall trends for Cu, Zn, Mn, Cd, Co, Ni and Sn in the sediment samples are similar. Values obtained from samples collected in winter were higher by a factor of about 1.5 than for samples collected in the summer months. The Co results, and to a lesser extent the Cd results, were erratic, and interpretation is difficult, but for the other elements, Cu, Zn, Mn, Ni and Sn, the smoothing obtained from the 3-cell rolling mean technique adequately displays this seasonal variation. The Fe and As results for the sediment samples show an opposite trend to those of Cu,

Zn, Mn, Ni and Sn, with values from samples collected in summer being higher in Fe and As by a factor of about 1.5 than for those collected in winter.

The water samples show a seasonal fluctuation in dissolved content of Cu, Zn, Fe and Mn, but not of Pb. All four elements which showed a variation exhibited their lowest values in the winter, and their summer values were higher by factors of 2.0 for Cu, 2.4 for Zn, 4.7 for Fe and 2.7 for Mn.

Thus, an antipathetic seasonal relationship between sediment and water was observed for Cu, Zn, and Mn, whilst the Fe contents of sediments and waters showed a sympathetic seasonal variation. The content of Ni and Sn in the sediments appeared to parallel that of Cu, Zn and Mn, as indeed did the Cd and Co contents, although the latter are difficult to interpret because of the erratic nature of the results. Arsenic in the sediments, however, appeared to follow a pattern very similar to that shown by Fe, which is not surprising in view of the close association between Fe and As (see Section 5.3.3., p.5.35, and Section 8.2.5., p.8.17).

These observations may be explained in terms of the groundwater and surface run-off system which feeds streams and rivers. During dryer periods, most water entering a stream will come from the groundwater. This water, having travelled slowly through the ground, possibly at considerable depth, may be expected to be metal rich, at least when compared with surface run-off water, which contributes substantially to the water content of streams in wet periods. It may thus be anticipated that stream waters will contain more metal in solution during the summer periods, when substantial contribution to the flow is made by the groundwater, than in the winter, when dilution by surface run-off may be expected to predominate over any increased groundwater flow. This is indeed born out by the Cu, Zn, Fe and Mn analyses of the water samples.

During periods of low rainfall, surface run-off is low, and therefore only small amounts of surface debris will be carried into the streams to contribute to the sediment load. It may be thus anticipated that the metal content of the sediments will be low during periods of low erosive capacity, i.e. the summer months, and higher during the winter, when surface run-off provides much more debris to add to the sediment load. This is shown by the analytical results of the sediment samples for Cu, Zn, Mn, Ni and Sn and in more erratic fashion by Cd and Co.

The only elements which do not demonstrate this form of variation in the sediment samples are Fe and As. Iron is present in sediments from Yarner Stream, below the mine, predominantly in the form of ferric hydroxide precipitate, often in a flocculent or jelly-like form. This material appears to have been precipitated in situ, as the effect of flooding is to wash it away, after which it builds up again gradually. Therefore the sympathetic seasonal variation in Fe content of the sediment and water may be due to the fact that in winter the stream water carries less Fe, and therefore precipitates less ferric hydroxide on the stream bed. Hem (1972) suggests a number of mechanisms which may control solubility of Fe in natural waters. Amongst those which he suggests (p. 449 and 450) are pH and water temperature. Although neither of these parameters were measured systematically each time samples were collected, they were measured on four separate occasions over the two year period. The values recorded are shown in Table 7.3.

TABLE 7.3 Temperature and pH values measured at YW 10 in Yarner Stream.

	<u>29.3.76</u>	<u>16.10.76</u>	<u>4.4.77</u>	<u>15.10.77</u>
Temperature (°C)	7.5	10.5	8.0	12.0
pH	5.9	5.2	5.8	5.4



It can be seen from the Table that water temperature varies by at least 4°C over a year, and that pH may well be higher in the winter by in excess of 0.5 units. The precise effects of temperature upon Fe solubility are not well understood, but an increase in pH of the stream water will cause a considerable decrease in Fe solubility, similar to that observed in the water samples collected in the winter. Whilst dilution of Fe rich groundwater by surface run-off undoubtedly occurs, pH controlled changes in Fe solubility may also contribute to a reduction in the rate of ferric hydroxide precipitation on the stream bed during the winter. In turn, this reduction may be responsible for the observed low Fe content of the sediments collected during the winter period. The intimate association of Fe with As, already referred to, may be responsible for the As values of the sediments following the same trend as the Fe values.

A rapid thaw followed heavy snowfall in Devon during February 1978, and extra water samples were collected on a daily basis during the floods which resulted. It was anticipated that the excess surface run-off, caused by the rapid melting of the snow, would result in the metal content of the waters falling considerably. Analysis of the water samples showed that, on the contrary, more metal was present in the flood water samples. Indeed, the range for Fe and Mn, shown by the flood water samples, is equivalent to the seasonal variation shown throughout the year. For Cu and Zn peaks in metal content were also detected, but only representing about half the annual variation.

When the relevant sample bottles were examined, it was found that samples collected during the floods contained very much more solid material than those collected during more normal discharge. Some bottles were shaken up and a fixed volume of water filtered. Attempts to weigh the resultant filtrate were thwarted by changes in moisture content of the filter papers themselves. Burning of ashless filter papers was not attempted because of the possibility that some of the suspended solid

matter might be organic and therefore would be destroyed by burning the papers. However, visual examination of the filter papers after filtering was sufficient to confirm the excess of solid material removed from the flood water samples (see Plate 11). Filter paper A was a sample from the floods, and B was a normal winter sample.

The extra force of the water when the stream was in spate was obviously sufficient to carry, in suspension and saltation, more solid material than normal, and the water sample probably leaches metal from this solid material after sample collection. Other samples, collected after periods of heavy rain, were also found to contain unexpectedly high quantities of metal (e.g. YWWS 34 for Cu, Zn and Mn, and YWWS 50 for Pb), and a similar explanation seems likely.

A number of elements, notably Cu, Zn and Sn, appear to be concentrated in some sediment samples collected after prolonged dry periods. For example, sample 22 contained 360 ppm Zn, 4 times the mean at that time of the year. It was, in fact, the first sample collected after rain fell, breaking the 5 week long completely dry spell in July and August 1976. This effect, however, is not demonstrated by all elements, nor is it shown by all samples collected after heavy rainfall.

Detailed variations in the metal content of both waters and sediments may be related to rapid climatic changes especially in rainfall levels. A striking inverse relationship is observed between potential evapotranspiration (Fig. 7.1) and Cu, Zn, Mn, Cd, Co, Ni and Sn content of the YWS series sediment samples and a parallel relationship with Fe and As. However, the plot of evapotranspiration for 1977-78 (Fig. 7.2) does not show the same obvious systematic variation and the usefulness of potential evapotranspiration as a parameter for climatic comparison is therefore called into question.

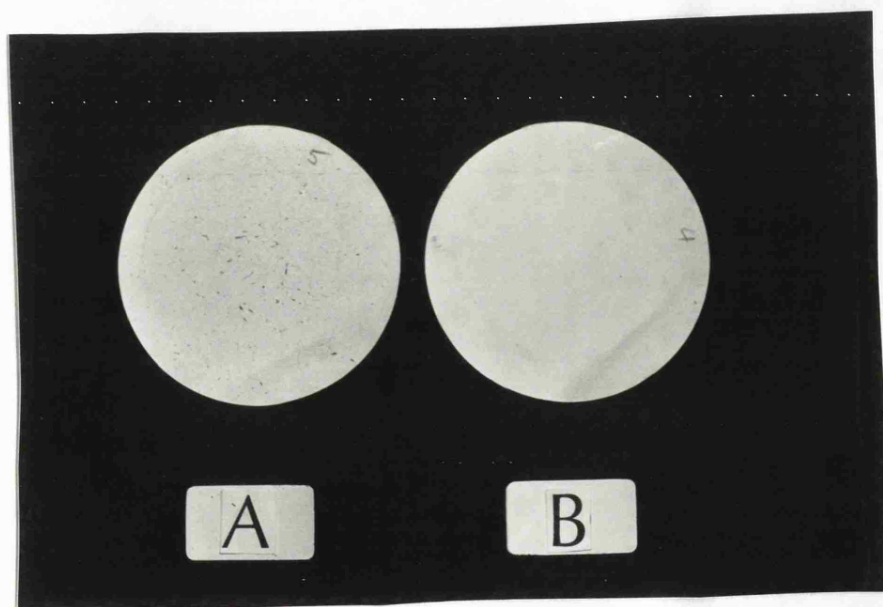


PLATE 11

Filter papers following filtration of:

(a) water sample taken during floods;

(b) water sample taken during normal winter flow.

## 7.5 CONCLUSIONS

Weekly sampling of sediments and waters, in an area of known mineralisation, was carried out, and the results demonstrate that seasonal variations, significantly in excess of total error variance for most elements did occur. Metal content of the sediments varied, from summer to winter, by a factor of about 1.5 with Cu, Zn, Mn, Ni and Sn, and to a less certain degree Cd and Co, having high values in the winter. Fe and As showed variation to a similar degree, but had high values in the summer. The Pb content of the sediments was apparently unaffected by the changing seasons.

Analysis of the water samples showed that seasonal variations occurred for Cu, Zn, Fe and Mn, but not for Pb. Samples collected in summer contained more metal than those collected in winter by factors ranging from 2.0 for Cu, to 4.7 for Fe. High values recorded from samples collected during times of flooding are attributed to the inclusion of more suspended solid material than usual in these samples. It is assumed that the acidified sample liquid is capable of removing metal from these solid particles.

The antipathetic relationship between sediments and water for Cu, Zn and Mn may be explained in terms of the relative importance of groundwater and surface run-off as a means of supplying water and detritus to a stream. When rainfall is light, metal-rich groundwater may be the dominant source of water in the stream and erosion of surface material by run-off may be very limited. This may result in the observed high metal values in the water samples collected in the summer, and the corresponding low values in the sediments. During the winter, high rainfall results in rapid surface run-off and fast surface erosion. This

may explain the lower metal values in the winter water samples, and the higher sediment values.

A sympathetic variation existed between water and sediment contents for Fe. This may have been the result of the possible in-situ precipitation of Fe as ferric hydroxide, with the result that the amount of Fe in solution may directly control the amount of Fe present in the sediment. The Fe content in the water may be affected by dilution by surface run-off in winter, and it may also be affected by apparent seasonal variations in pH and/or temperature of the water. Further detailed work of this nature should include measurement of pH, temperature and possibly also Eh and conductivity. The chemical affinity of As for ferric iron probably accounts for the similarity in the Fe and As contents of the sediments.

The magnitude of seasonal variation observed in the sediment samples is unlikely to affect the interpretation of results from a mineral reconnaissance programme designed to isolate "sore thumb" anomalies. However, future trends in applied geochemistry must be increasingly towards the search for mineral deposits whose geochemical expression is more subtle. As this trend develops, variations of the type described in this chapter will have to be considered more and more seriously. As Webb et al. (op. cit.) point out, applied geochemistry has an increasingly significant part to play in the field of geochemical mapping, not simply as an end in itself, but as an aid to geological mapping, as well as in such fields as medical, veterinary and agricultural geography. Seasonal variations of the magnitude described in this Chapter may have to be considered during evaluation of results obtained for such purposes.

The development of flame-less atomisation techniques in AAS has already resulted in the lowering of detection limits, for many elements, to levels where significant background variations in metal content of natural waters can be detected. A case has already been put (Section 6.4, p.6.27) for the use of water as a regional sampling medium. The advantages are that it is largely free from sampling errors, and entirely free from sub-sampling errors. If the levels of seasonal variation reported from the present study are subsequently shown to apply more widely, they are of sufficient magnitude to affect the results of a regional stream water sampling programme. It is clear, from the results obtained, that less erratic changes in metal content are observed in samples collected during the summer months, when rainfall is at a minimum. Therefore, if it is considered that water sampling has a wider potential application than just as a follow-up sampling medium, collection during periods of rapidly fluctuating groundwater and surface water levels must be avoided. Due account must be taken of seasonal fluctuations, possibly by recourse to regular re-sampling of a number of localities throughout the period of investigation.

The variations described in this Chapter are in no instance less than the total error variation for similar samples from the same locality, and in most cases they are significantly greater. Therefore, a significant loss of reproducibility may be introduced into data from samples collected at different times of the year and, under certain circumstances even when collected within a limited period of time. This may seriously affect attempted comparisons of data sets drawn from different sources.

## CHAPTER 8

### DETAILED EVALUATION OF YARNER WOOD AREA

#### 8.1 INTRODUCTION

#### 8.2 RESULTS AND INTERPRETATIVE TECHNIQUES

##### 8.2.1. Stream sediments, hot extractable metals

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8.2.1.3. Lead

8.2.1.4. Zinc

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##### 8.2.2. Stream sediments, cold extractable metals

##### 8.2.3. Water samples, pH, Eh, conductivity and dissolved oxygen content

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8.2.3.2. pH measurements

8.2.3.3. Eh measurements

8.2.3.4. Conductivity

8.2.3.5. Dissolved oxygen content.

##### 8.2.4. Soil samples

##### 8.2.5. Cluster analysis

#### 8.3 CONCLUSIONS

## CHAPTER 8

### DETAILED EVALUATION OF YARNER WOOD AREA

#### 8.1 INTRODUCTION

The main purpose of most of the sample collection carried out in the National Nature Reserve at Yarner Wood, near Bovey Tracey, was to obtain sets of samples upon which assessment of errors and adapted techniques could be based. Inevitably, during the course of evaluation of this data, an overall picture of the metal dispersion, in relation to mineralisation, began to emerge, and some of the sediment and water sampling, and all of the soil sampling, was carried out specifically to further an understanding of secondary dispersion related to mineralisation.

Regional sediment sampling in the south Dartmoor region has shown that sediment from Yarner Stream, sampled near to locality YW1 (see Fig. 1.2) persistently contained anomalous quantities of Cu and Zn (C.H. James, pers. comm.). Detailed follow-up sediment sampling by Harrison (1974) confirmed this and related the anomalous metal to the presence of old mine workings at 27830783, although it was noted that a small right-bank tributary, flowing into the main stream at 27780774, appeared to be a major source of Zn and Mn. During the initial phases of the present investigation 152 sediment samples were collected from 88 localities. At the time of sample collection the pH, Eh, conductivity and temperature of the water at most sample sites was measured. Dissolved oxygen content was also measured at a few localities.

Following the successful application of available analytical techniques to water samples, 26 localities in Yarner Wood were chosen for water sample collection. Sediment samples from the same localities were selected for analysis for cold extractable metals. Two traverses



were completed during which soil samples were collected, at 25m intervals, in order to see if indications (drawn from the stream sediment and water samples) concerning the strike and extent of mineralisation could be confirmed by soil sample analysis.

The geology of the immediate area is fairly simple. The 1 inch to 1 mile Geological Survey map shows the main part of Yarner Wood to be underlain by shales of Carboniferous age, and outcrops within the National Nature Reserve confirm this. Late Pliocene outwash, from the rapid erosion of the granite to the north and west, formed deposits known as the Bovey Beds. Further south these form the clay deposits of the Bovey Basin, but, in their proximal facies, they are medium to coarse sands, composed largely of quartz and feldspar grains. They are shown by the Geological Survey to underlie Yarner Stream between the Lodge (27860788) and the River Bovey confluence (27950798). They may, indeed, form a thin surface veneer over that whole area, but shales outcrop in the stream bed as far downstream as locality 77 (see Fig. 1.2) at 27900792. Downstream of this point, granitic material, derived from the Bovey Beds, is evident in the stream bed load, and is the sole source of material in sediments from the tributaries sampled at localities 80 and 81.

Extensive dumps occur in the vicinity of the main shaft of Devon Wheal Frances at 27830784 and numerous collapsed adits can be seen between the dumps and locality 63 (27770783) where a strong, Fe rich spring rises from the material infilling an old adit entrance. Records concerning the mine are sparse as production, begun in 1858, lasted for only 7 years. However, the material on the dumps shows the ore to have contained pyrite, chalcopyrite, and smaller quantities of pyrrhotite, sphalerite and arsenopyrite.

## 8.2 RESULTS AND INTERPRETATIVE TECHNIQUES

### 8.2.1. Stream sediments, hot-extractable metals

#### 8.2.1.1. Introduction

Analysis for Cu, Pb, Zn, Fe, Mn, As, Cd, Co and Ni by AAS followed digestion of 0.5g of minus 125 micron material in 5 ml of 4M HNO<sub>3</sub> for 4 hours at 95°C. All samples were diluted to 10 ml with 0.5% lanthanum chloride solution, homogenised and decanted into sealable glass containers prior to analysis.

For every element but Cd, it was demonstrated in Table 3.3 (p.3.9) that analytical and sub-sampling errors are small compared with sampling errors. Therefore, interpretational techniques which involve statistical smoothing to reduce the effects of analytical and sub-sampling errors, are an unnecessary complication. One of the simplest forms of interpretation is the plotting of profiles showing position on a traverse as the independent variable, and the metal content of samples as the dependent variable. This is readily applicable, in two dimensions, to soils, where samples have been collected on straight line traverses, but three dimensions appear to be necessary if this technique is to be applied to stream sediment data, since two dimensions are necessary to show the geographical location, and then a third for the metal values. An attempt has been made to overcome this by, firstly, straightening out the plot of the stream course and, secondly, displacing tributary and distributary streams (such as the Pottery Leat) above or below the main stream (see Fig. 8.1). Metal content, stream water pH and conductivity are shown, using this technique, in Figs. 8.2 to 8.12 inclusive, and comparison of these plots with Figs. 1.2 and 8.1 re-introduces the extra dimension of the geographical location.



#### 8.2.1.2. Copper

The results of Cu analysis on all samples collected are shown in Appendix 3, and the results of the routine samples (1 sample per locality) are shown in Appendix 4. These results are displayed graphically in Fig. 8.2, from which a number of points may be deduced. All the headwater streams, including the spring at locality 63, were low in Cu (approx. 150 ppm), within the context of this stream basin, and the first significant input of Cu came from the mine dumps which contribute to the sediment load at locality 32, although the Fe rich sediment precipitated by the water flowing from a collapsed adit at locality 27 was not Cu rich. The results suggest that inputs of Cu into the stream also occur near localities 17 and 10 in the main stream and 127 in the Leat distributary.

Dilution by barren material from the Woodcock Stream is obvious below the confluence, and further dilution occurs as the stream flows over the Bovey Beds, downstream of locality 80. However, there was still a pronounced 10 fold contrast between the River Bovey (22 ppm) and Yarner Stream (225 ppm) at their confluence.

#### 8.2.1.3. Lead (Appendices 3 & 4; Fig. 8.3)

High Pb values (above 100 ppm) only occurred in the right bank tributaries which drain the south west of the headwater region, including Yarner Farm (27750782). The spring at locality 63 was not however, a source of Pb. This pattern of high Pb values was progressively diluted downstream giving rise to a smooth decay of the anomaly pattern. Dilution caused by the presence of the Bovey Beds can be seen around locality 79, and contrast between the Yarner Stream (24 ppm) and the River Bovey (22 ppm) was lost.

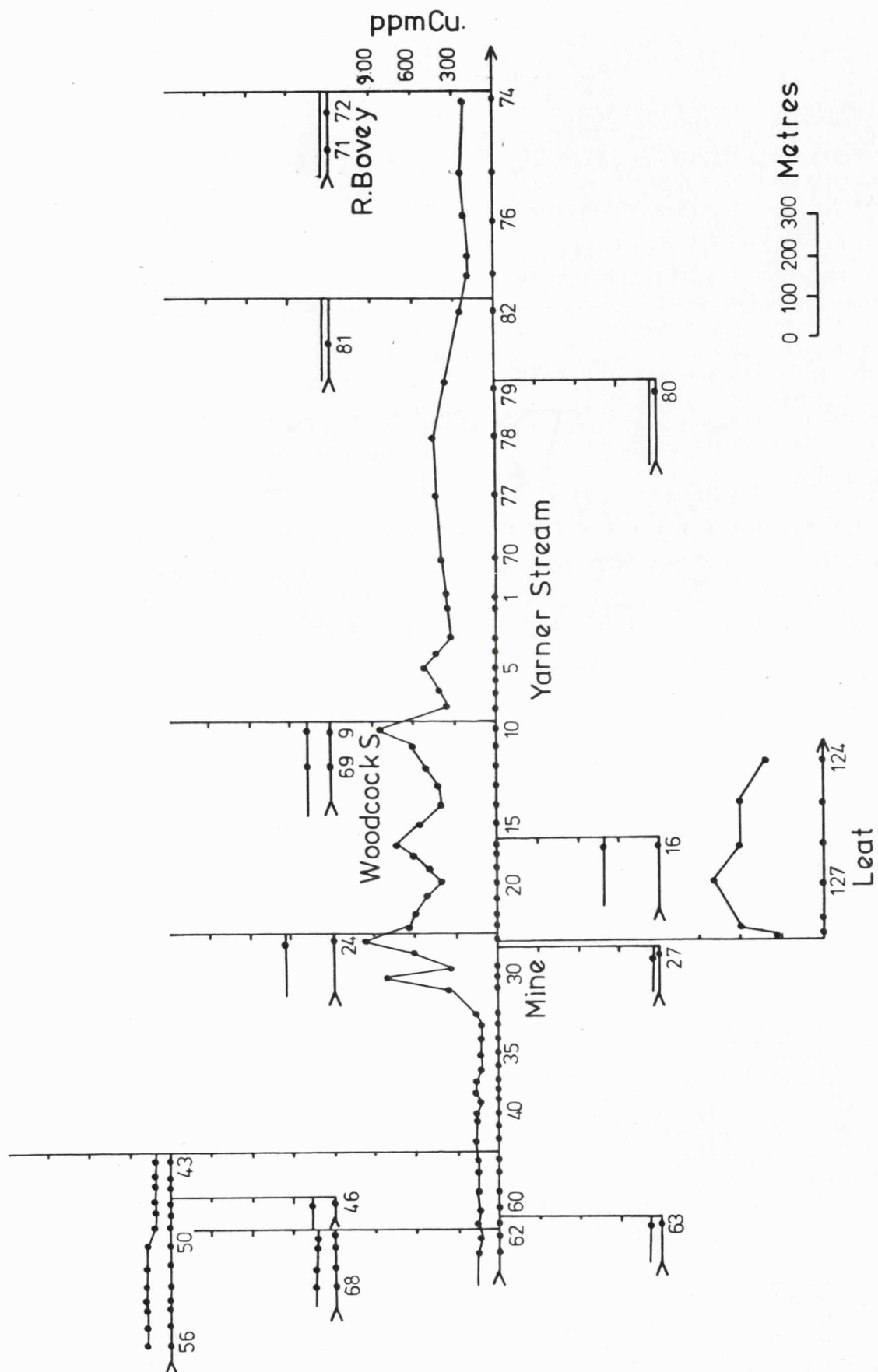


FIG.8-2 SCHEMATIC PLOT OF Cu CONTENT OF SEDIMENTS  
IN YARNER WOOD AREA.

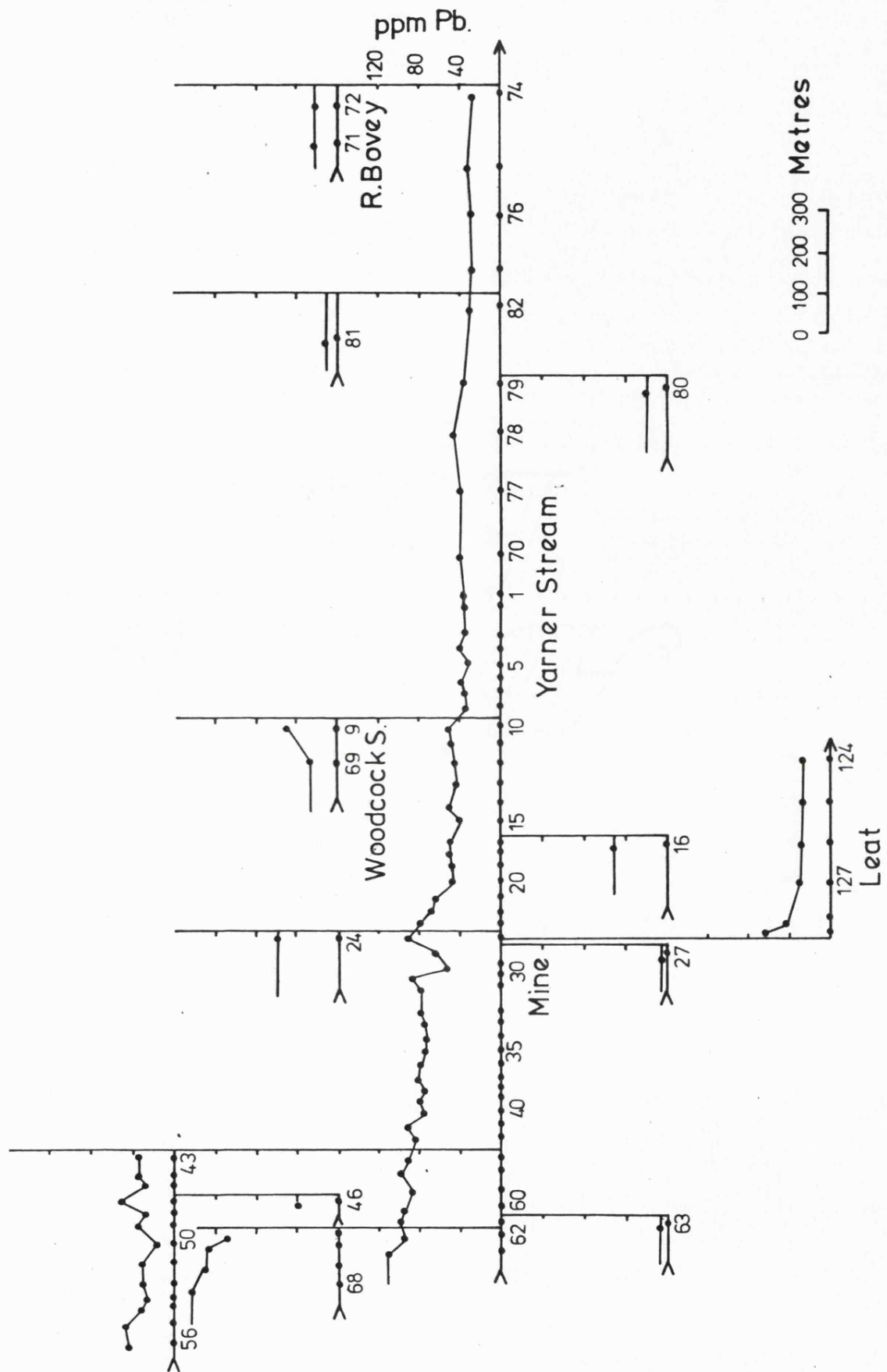


FIG. 8.3 SCHEMATIC PLOT OF Pb CONTENT OF SEDIMENTS  
IN YARNER WOOD AREA.

## 8.2.1.4. Zinc (Appendices 3 &amp; 4, Fig. 8.4)

The tributaries which flow through localities 68 and 62 were both relatively high in Zn (>300 ppm), and the spring at locality 63 was a very prominent Zn source. The main headwater branch of Yarner Stream, passing locality 50, was, by comparison, very low in Zn. Below the confluence, between locality 42 and the mine, the Zn content remained fairly constant at about 600 ppm, and below the mine the Zn fell below 300 ppm. A 2.6 fold contrast remained, however, between Yarner Stream (162 ppm) and the River Bovey (62 ppm) at their confluence.

Of interest is the sample from locality 25, between the Leat distributary and the locality 24 stream confluence. This sample, containing 1180 ppm Zn, came from a stagnant pool of water, so caused by diversion of the majority of the stream flow into the Leat (see Plate 12). The sediment in this pool was very strongly Mn stained (see Plate 13), and the high Zn value may relate to changes in pH/Eh of the stream brought about by the stagnancy, rather than an influx of Zn into the system at that point, although the sample point is next to a small, overgrown, wasteheap.

## 8.2.1.5. Iron (Appendices 3 &amp; 4, Fig. 8.5).

The headwater tributaries were low in Fe, but sediment from the spring, at locality 63, contained 180,000 ppm Fe. Some input of Fe into the main stream is also observable below locality 50. Between localities 42 and 30 there was a gradual decrease in the anomaly caused by the spring at locality 63, from approximately 60,000 ppm to 30,000 ppm.

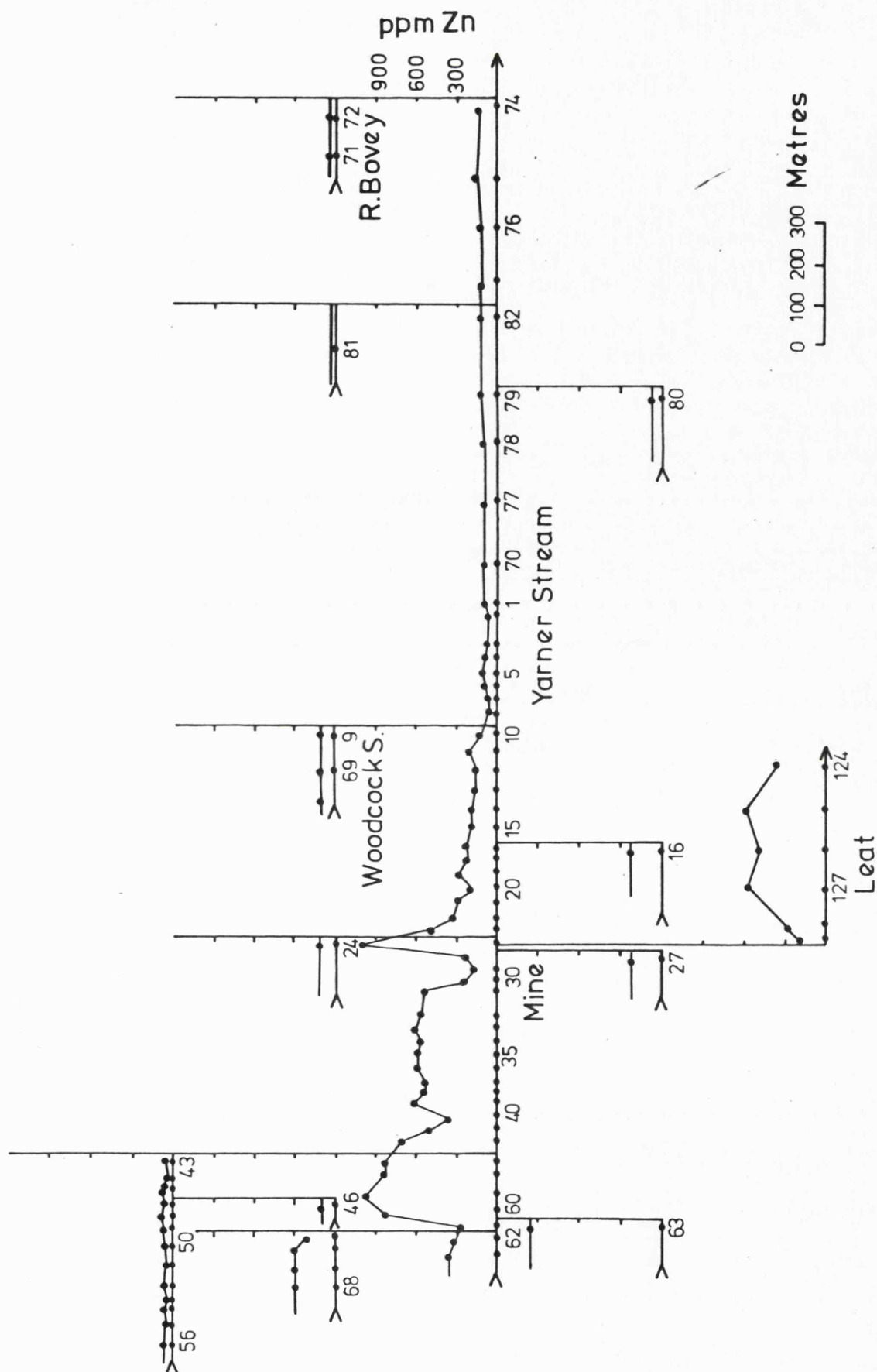
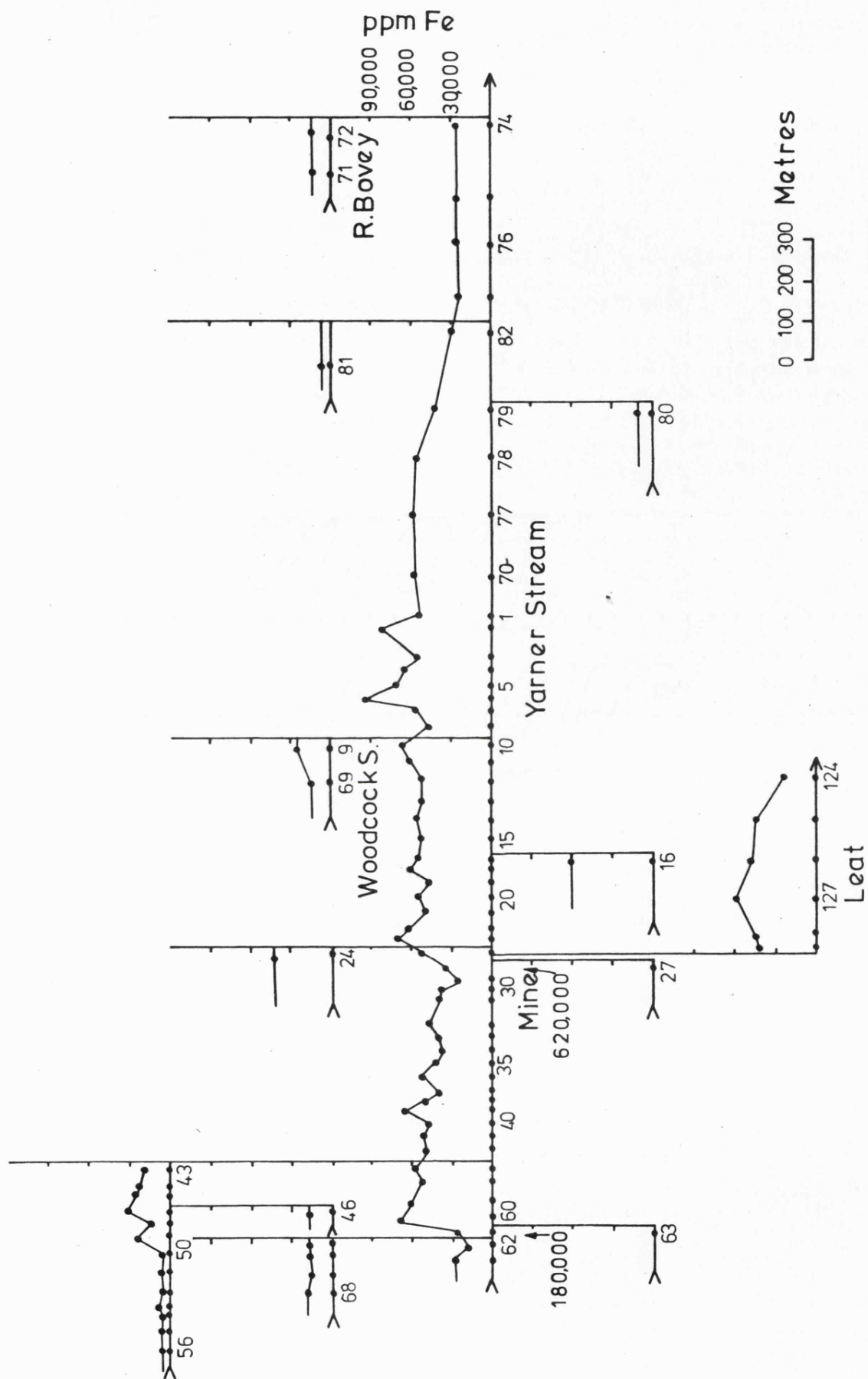


FIG. 8.4. SCHEMATIC PLOT OF Zn CONTENT OF SEDIMENTS IN YARNER WOOD AREA.





**FIG. 8.5** SCHEMATIC PLOT OF THE Fe CONTENT OF SEDIMENTS IN YARNER WOOD AREA.



Plate 12      The Pottery Leat distributary channel at locality YW 26,  
Yarner Wood.



PLATE 13

Manganese-stained sediment in stagnant pool at locality  
YW 25 in Yarner Wood.

Sediment collected at locality 27 was almost pure ferric hydroxide, being 62% Fe. Below the mine, the stream bed was covered with Fe rich precipitate and the sediments maintained an Fe content of approximately 60,000 ppm until dilution, caused by the presence of the Bovey Beds at about locality 79, reduced the Fe content to approximately 25,000 ppm, which represents a two-fold contrast with the River Bovey (11,700 ppm).

#### 8.2.1.6. Manganese (Appendices 3 & 4, Fig. 8.6)

The headwater streams were all low in Mn, but sediment from locality 63 contained 19000 ppm and gave rise to the anomaly which can be seen to be decaying slowly, if a little erratically, between localities 42 and 32. The effect upon this dispersion pattern of the mine is to cause a decrease below 3000 ppm. The sample from locality 25 was high in Mn (7700 ppm) and reasons for this were considered in Section 8.2.1.4 (p.8.5). A contrast by a factor of 3.7 was present between Yarner Stream (1010 ppm) and the River Bovey (270 ppm) at their confluence.

#### 8.2.1.7. Arsenic (Appendices 3 & 4, Fig. 8.7)

The headwater streams were low in As, whilst the spring at locality 63 contributed 14000 ppm giving rise to an anomaly pattern which decayed from 4400 ppm at locality 59 to 2440 ppm at locality 32. The spring at locality 27 was another source of As (10,900 ppm), and high values at localities 18 and 15 (7000 and 8200 ppm respectively), may be related to mineralisation. The presence of the Bovey Beds, downstream from locality 78, caused a drop in As content from 2340 ppm to about 800 ppm. However, a ten-fold contrast was still observable between the Yarner Stream (760 ppm) and the River Bovey (80 ppm).

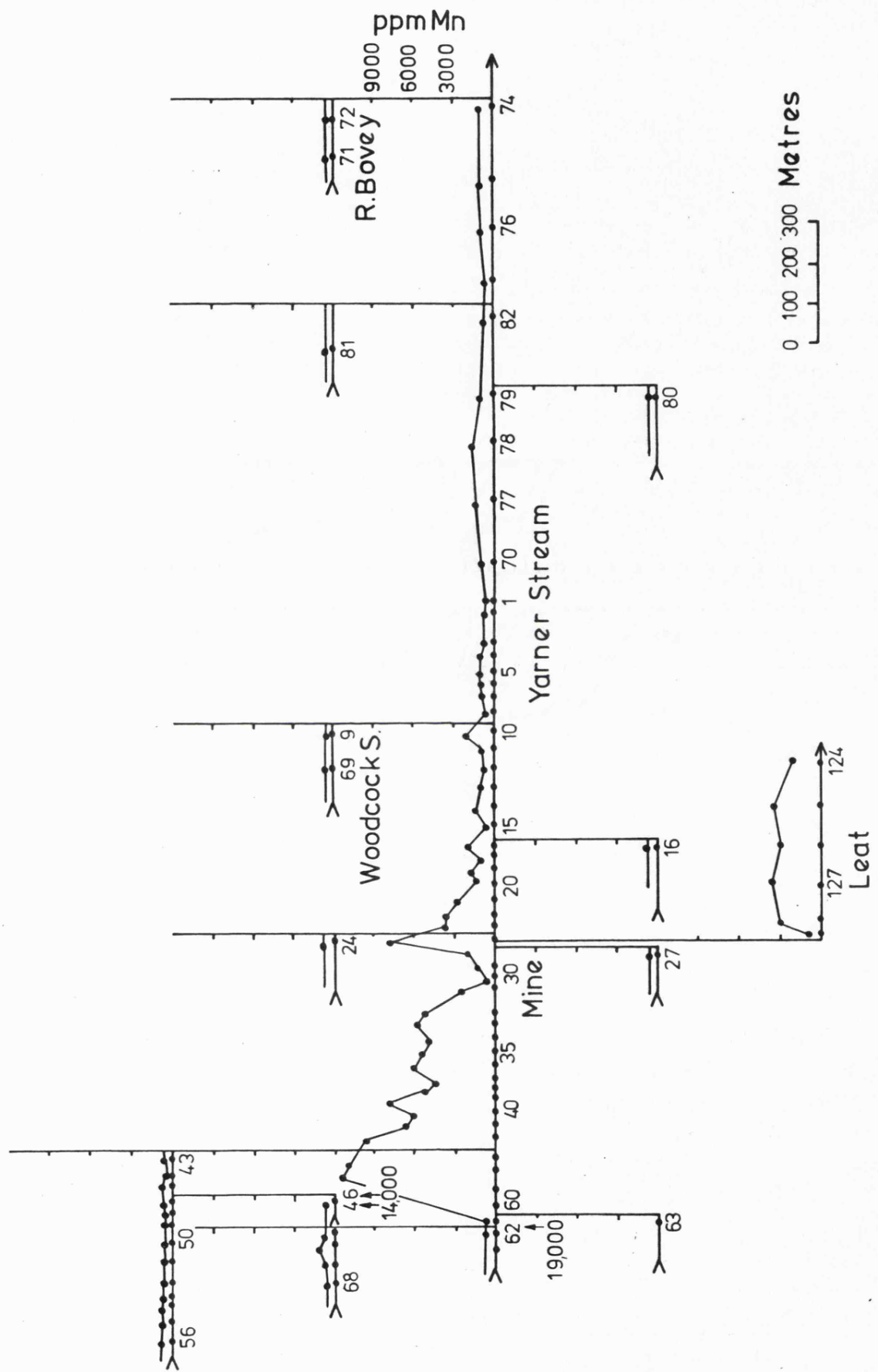


FIG 8.6

SCHEMATIC PLOT OF Mn CONTENT OF SEDIMENTS  
IN YARNER WOOD AREA

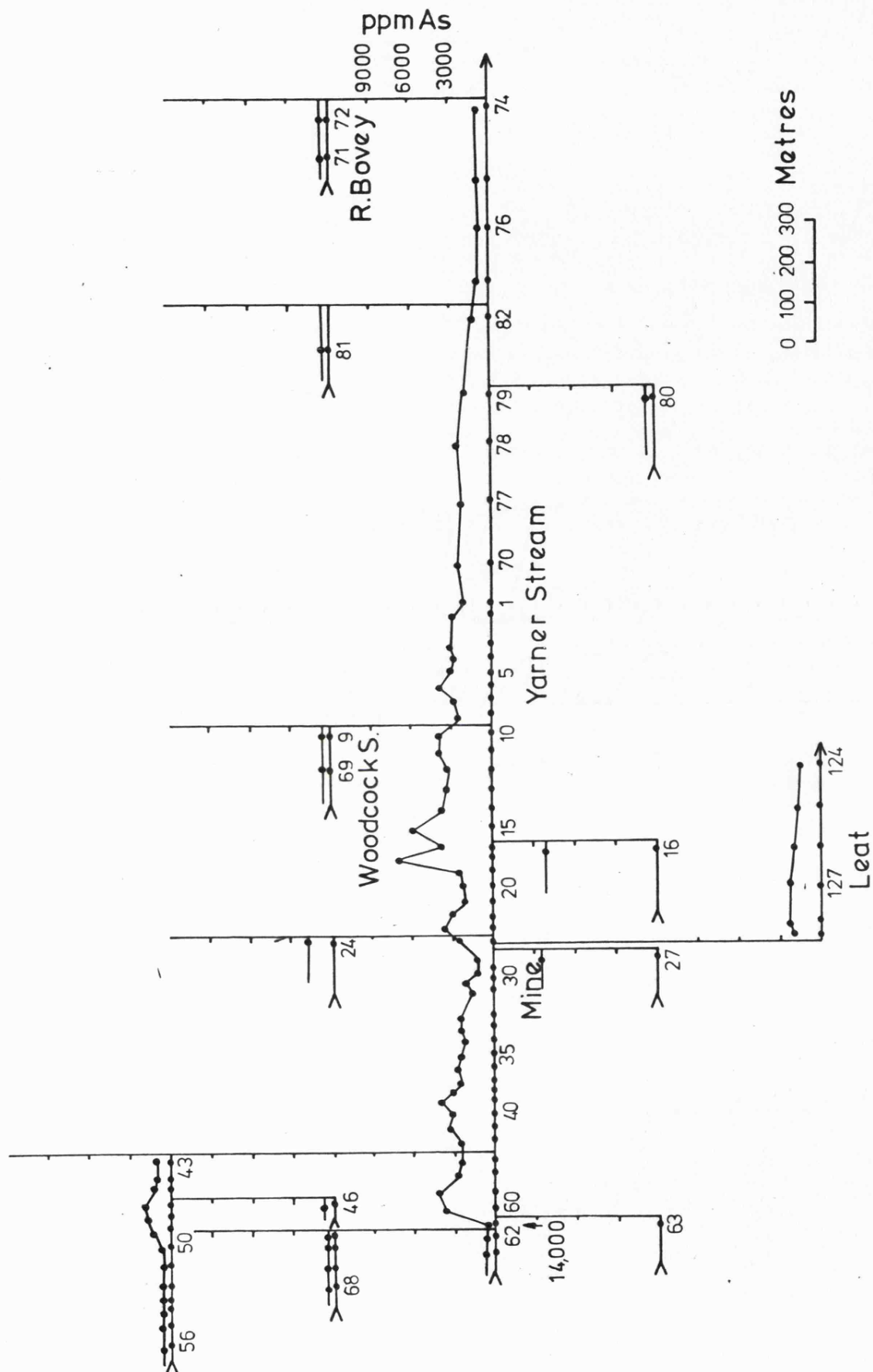


FIG. 8.7 SCHEMATIC PLOT OF As CONTENT OF SEDIMENTS  
IN YARNIER WOOD AREA.



#### 8.2.1.8. Cadmium (Appendices 3 & 4, Fig. 8.8)

Mention was made in Section 3.2.2.3. (p.3.7), that discussion of the Cd results could only be of a qualitative nature because of the close approach of most of the results to the detection limit. Worth mention, however, are two features shown by Fig. 8.8. Firstly, the Cd content of sediments upstream of the mine was generally higher than for samples downstream. Secondly, the sample from locality 25 was high in Cd (10.5 ppm) as it was for Zn and Mn.

#### 8.2.1.9. Cobalt (Appendices 3 & 4, Fig. 8.9)

Of particular interest in the Co results is that the samples in the headwaters of Yarner Stream, upstream of locality 50, were high in Co, reaching a maximum of 178 ppm at locality 55. The small right bank tributary at locality 46 was found to be a large Co source, containing 192 ppm, the highest value recorded in Yarner Wood. Locality 63 proved to be a moderate Co source, contributing 93 ppm, whereas the headwater streams from localities 68 and 62 were very low (approximately 20 ppm). The effect of the mine was to cause a decrease in Co content, shown by low values at localities 31,30,29 and 28, whilst again locality 25 proved to be high, as it was for Zn, Mn and Cd. Downstream from the mine, values were more erratic than upstream, possibly due to Co being added to the system from mineralisation. A ten-fold contrast was present between Yarner Stream (81 ppm) and the River Bovey (8 ppm) at their confluence.

#### 8.2.1.10. Nickel (Appendices 3 & 4, Fig. 8.10)

The sediments from the headwater streams were all low in Ni, but material from locality 63 was high (200 ppm) and persistently high values (approximately 150 ppm) were recorded down the main stream as far as

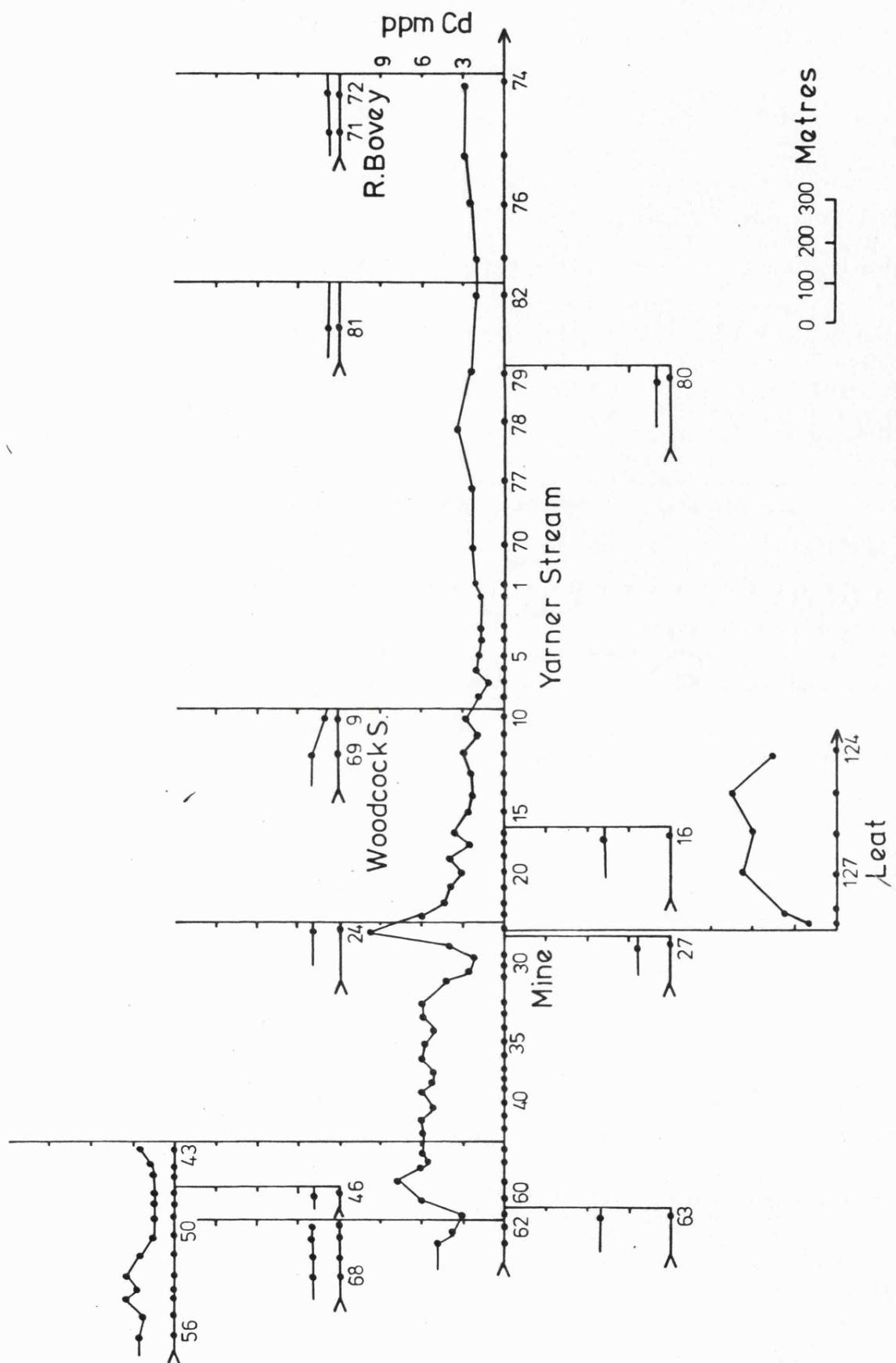


FIG. 8.8 SCHEMATIC PLOT OF Cd CONTENT OF SEDIMENTS  
IN YARNER WOOD AREA



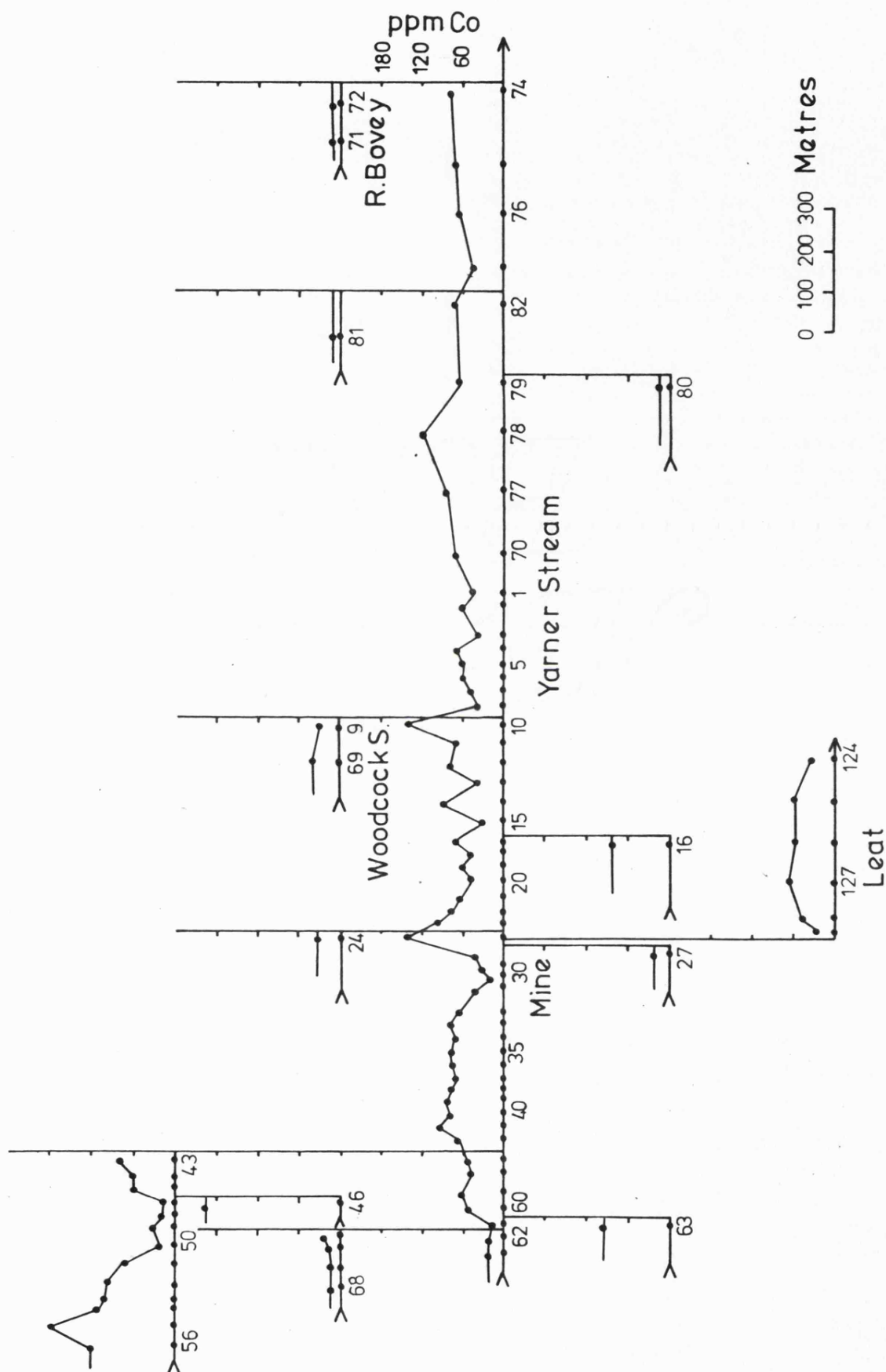


FIG 8.9 SCHEMATIC PLOT OF Co CONTENT OF SEDIMENTS IN YARNER WOOD AREA.

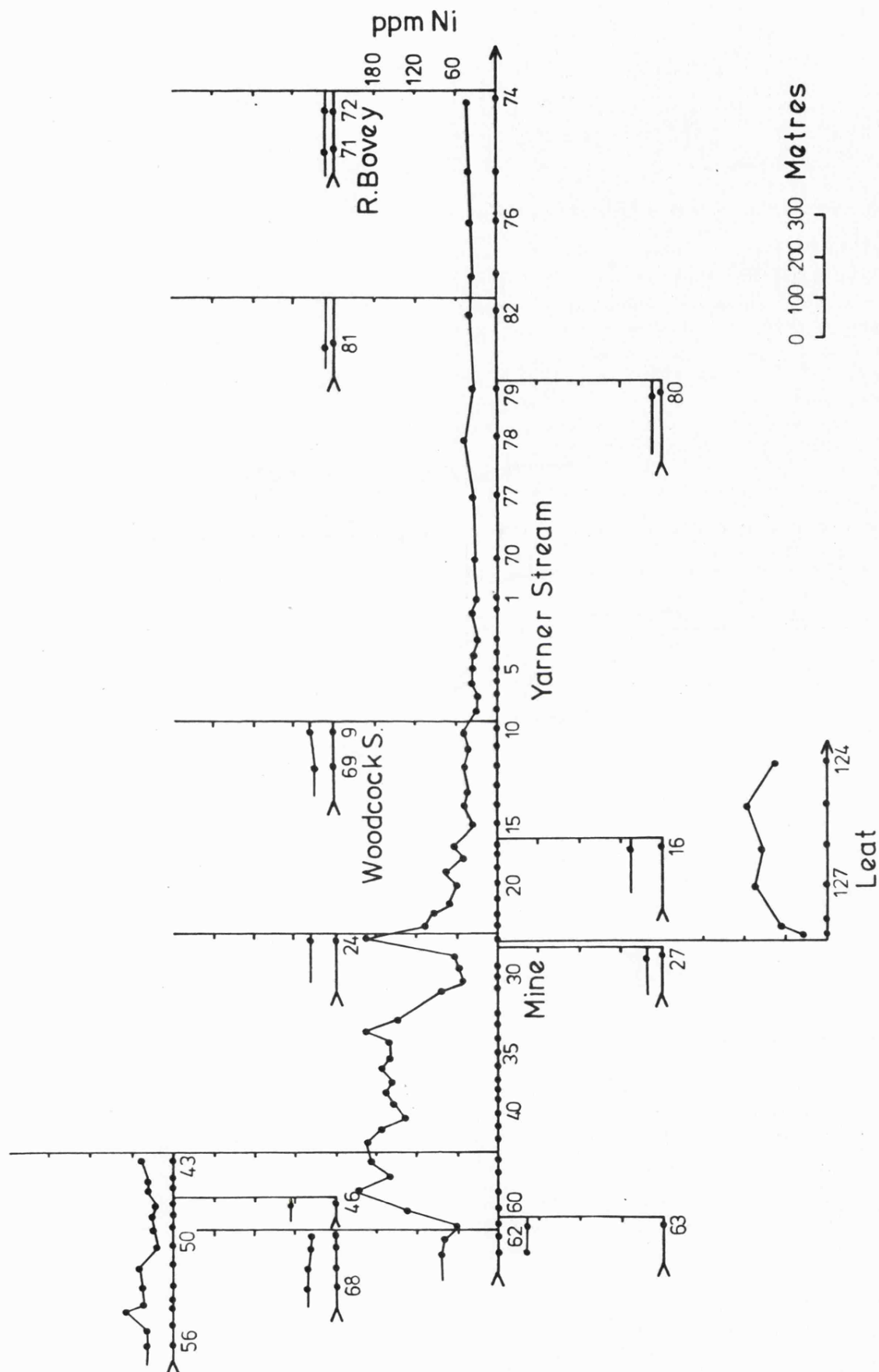


FIG. 8.10 SCHEMATIC PLOT OF Ni CONTENT OF SEDIMENTS  
IN YARNER WOOD AREA.

locality 32. At, and downstream of the mine lower values were recorded (approximately 40 ppm) with the exception of the material from locality 25, which contained 196 ppm. A four-fold contrast was present between Yarner Stream (47 ppm) and the River Bovey (11 ppm).

### 8.2.2. Stream sediments, cold extractable metals

Sediment from 26 localities was selected for cold extractable (cx) metal analysis. 0.5g of sample was shaken for 30 seconds, on a Whirlimixer, in 10 ml of 10% (w/v) ammonium citrate/hydroxylammonium chloride solution, allowed to settle, decanted, and analysed by AAS for Cu, Pb, Zn, Fe, Mn, Cd, Co and Ni. The analyses are shown in Table 8.1 and the general patterns are similar to those shown by the hot extractable (hx) results, although some notable differences may be observed. For example, the peaks in the Cu content shown by material from localities 10 and 17 were more clearly shown by the cx results. The cx Cu content for locality 10 was twice that for locality 12, whilst the ratio for the hx results was about 1.5. In addition, the contrast between Yarner and Woodcock streams (mineralised and background respectively) is more clearly demonstrated by the cx results (see Table 8.2).

TABLE 8.2 Comparison of metal content in Yarner Stream (locality 10) and Woodcock Stream (locality 9) by hx and cx results.

	hx (ratio sample 10:sample 9)	cx (ratio sample 10: sample 9)
Cu	4.6	11.5
Pb	0.9	1.2
Zn	1.5	3.1
Fe	2.7	2.7
Mn	11.0	11.6
Cd	3.0	3.0
Co	5.7	14.3
Ni	2.2	5.0

TABLE 8.1

Cold extraction analytical results, Yarner Wood sediment samples.

YARNER WOOD COLD EXTRACTION, 8 ELEMENTS, ALL IN PPM

LOCALITY	CU	P3	ZN	FE	MN	CO	CO	NI
9.	24.0	4.0	15.0	400.0	180.0	.5	5.0	3.0
10.	27.0	5.0	50.0	1000.0	2000.0	1.5	85.0	15.0
12.	142.0	1.0	59.0	700.0	1320.0	1.0	51.0	17.0
14.	32.0	2.0	45.0	630.0	1180.0	1.0	49.0	11.0
16.	56.0	.1	34.0	230.0	360.0	1.0	25.0	9.0
17.	134.0	3.0	84.0	820.0	1800.0	1.5	40.0	20.0
19.	90.0	5.0	85.0	640.0	1440.0	1.5	29.0	21.0
23.	158.0	6.0	164.0	970.0	3300.0	2.5	51.0	37.0
26.	72.0	4.0	50.0	620.0	840.0	.5	13.0	12.0
27.	1.0	.1	51.0	2500.0	560.0	.2	26.0	6.0
28.	144.0	11.0	126.0	630.0	1920.0	2.0	21.0	27.0
33.	27.0	15.0	300.0	1300.0	5200.0	4.0	43.0	92.0
43.	10.0	4.0	21.0	520.0	480.0	.5	27.0	18.0
46.	11.0	3.0	34.0	420.0	500.0	.5	71.0	20.0
47.	5.0	1.0	10.0	540.0	80.0	.5	4.0	7.0
57.	28.0	19.0	425.0	2240.0	9600.0	4.0	29.0	108.0
58.	24.0	19.0	415.0	2140.0	9500.0	3.0	27.0	86.0
60.	25.0	16.0	355.0	2450.0	11200.0	3.0	29.0	77.0
62.	12.0	24.0	95.0	400.0	860.0	1.5	8.0	24.0
63.	158.0	.1	995.0	4000.0	35000.0	4.5	94.0	160.0
64.	6.0	25.0	70.0	380.0	480.0	.5	3.0	8.0
124.	120.0	4.0	160.0	540.0	1420.0	2.0	20.0	28.0
125.	217.0	6.0	205.0	1010.0	2780.0	4.0	37.0	51.0
126.	100.0	5.0	211.0	320.0	2120.0	2.5	32.0	34.0
127.	223.0	5.0	225.0	1070.0	2420.0	2.5	33.0	36.0
128.	181.0	8.0	111.0	1050.0	1680.0	1.5	27.0	21.0

It may thus be concluded that considerably more of the anomalous Cu,Zn,Co and Ni in locality 10 material was in a loosely held, cold extractable form than in the Woodcock Stream at locality 9.

Sufficient extra information appears to be available from the results of cx analysis to merit its inclusion in detailed follow-up work, and had more time been available, the present study would have been extended to include cx analysis of all 152 samples collected.

### 8.2.3. Water samples, pH,Eh, conductivity and dissolved oxygen content

#### 8.2.3.1. Water samples.

The localities chosen for cx analysis were also selected for water sample collection, and acidified water samples were collected in polythene bottles on October 16th 1977. All the samples were analysed directly by AAS, for Zn,Fe and Mn by flame atomisation and for Cu,Pb, As,Co and Ni by flameless atomisation (see Chapter 6). The results expressed in nanograms per millilitre, are shown in Table 8.3.

A number of features shown by the sediment results were confirmed by the water samples. For example, the inflows of Cu into the stream between localities 19 and 17 and between 12 and 10, were confirmed and the Pb anomaly, detected in the sediment results for locality 64 was also confirmed by the water analyses. However, one striking contrast with the sediment values was observed. The Zn,Fe,Mn,Co and Ni contents of the water sample from locality 33, assumed to be representative of the stream between localities 42 and 30, were all very low. This is in contrast, firstly with the higher metal content of water samples collected downstream of the mine, and secondly with the high metal values in sediments from both the same site and upstream from the mine. It thus seems

TABLE 8.3

Analytical results, Yarner Wood water samples.

LOCALITY	CU	P3	ZN	FE	MN	AS	CO	NI
9.	6.0	.4	2.0	200.0	7.0	5.5	.8	.2
10.	53.0	.4	109.0	975.0	70.0	31.0	9.2	23.0
12.	37.0	1.1	93.0	750.0	77.0	31.0	7.0	10.5
14.	43.0	.6	142.0	1100.0	80.0	47.5	7.0	19.5
16.	7.0	2.3	33.0	25.0	7.0	10.5	.6	.2
17.	63.0	.4	108.0	1050.0	90.0	63.0	8.0	11.0
19.	13.0	.5	32.0	1350.0	152.0	39.0	4.0	10.5
23.	15.0	.5	11.0	2400.0	125.0	105.5	2.8	8.5
26.	27.0	1.3	37.0	1425.0	67.0	62.5	2.0	12.5
27.	.5	.4	117.0	6800.0	252.0	220.0	13.2	21.5
28.	10.7	.4	27.0	50.0	17.0	22.0	.6	4.0
33.	.3	.2	1.0	25.0	5.0	17.0	.2	.2
43.	.4	.3	1.0	25.0	2.0	3.0	2.4	6.0
46.	5.5	.4	17.0	775.0	50.0	36.5	12.5	13.0
47.	3.0	.5	15.0	1200.0	22.0	58.0	1.8	10.5
57.	3.0	.3	1.0	25.0	22.0	1.0	.4	6.0
58.	4.6	2.7	8.0	750.0	155.0	79.0	.8	3.0
60.	3.6	2.3	9.0	500.0	132.0	17.5	.1	1.0
62.	2.4	1.5	1.0	25.0	2.0	7.0	.1	.2
63.	4.5	.6	7.0	3750.0	490.0	86.0	.2	.5
64.	10.5	2.3	22.0	250.0	55.0	9.0	.1	1.0
124.	12.0	.5	26.0	150.0	16.0	11.0	.1	.5
125.	16.0	1.0	23.0	250.0	25.0	1.0	.1	2.0
126.	18.0	1.4	43.0	700.0	25.0	44.0	.1	.5
127.	10.0	.9	34.0	450.0	30.0	24.0	.1	5.0
128.	13.0	.9	25.0	450.0	22.0	35.0	.1	3.5

YARNER WOOD WATERS. 3 ELEMENTS, ALL IN NANOG/ML.

that above the mine the aforementioned metals are insoluble and trapped in sediments, whilst below the mine more metal is released from sediment into solution. This may be a pH controlled factor, as Fig. 8.11 demonstrates.

#### 8.2.3.2. pH measurements.

The pH of the stream was measured directly using a pH meter. It was found that upstream from the mine dumps, the water had a pH of 7.0 or greater, whilst at locality 32, the pH had fallen to 6.7, at locality 30 it was down to 6.5, and fell to a minimum of 5.9 at locality 10.

#### 8.2.3.3. Eh measurements.

Attempts were made to measure Eh directly. A 1/300 M potassium ferrocyanide and potassium ferricyanide buffer was used, which, according to Zobel (1946) has an Eh of 0.43 volts at 25°C. Numerous problems were encountered during attempts to measure Eh. For example, the electrode appeared to retain a "memory" of the buffer solution for some time after checking. This gave rise to high values immediately after checking the buffer, with slowly decreasing readings in subsequent measurements. Prolonged rinsing after reading the buffer was not sufficient to prevent this. Two different Eh meters were used at different times, which at the same localities, gave results up to 0.2v different, and patterns of results which did not correspond to one another. The proximity of an operating pH electrode whilst Eh readings were being made was found to feed a spurious voltage into the Eh cell. Therefore, the readings of Eh obtained were not used in the interpretation of the results, but in view of the importance of Eh on metal solubility it is a property of the secondary environment to which more attention should be devoted.





#### 8.2.3.4. Conductivity.

A simple bridge was used to measure stream water conductivity. The conductivity coefficient of water, determined experimentally to be  $1.7\%/^{\circ}\text{C}$ , was used to construct graphs which allowed compensation of the conductivity measurements made in the field to a standard temperature ( $25^{\circ}\text{C}$ ). All values of conductivity quoted refer to  $G_{25}$  (standardised) values measured in micro mhos/cm. ( $\mu\text{mho/cm.}$ ).

Fig. 8.12 shows a plot of conductivity values ( $G_{25}$ ) from Yarner Wood measured during early April 1976. Of particular interest is the effect of the spring at locality 63, and the dilution caused when the streams from localities 50 and 60 join and at the Yarner and Woodcock Streams confluence. The mine workings, and the dumps, have no effect upon conductivity values, although a peak in conductivity was observed between localities 19 and 13. However, as shown by the pecked line on Fig. 8.12, this anomaly was not reproduced when the stream was re-measured the following year. It is possible that the pattern observed in 1976 was real and not picked up in 1977. However, unexpected, high readings, obtained elsewhere at a later date, were found to be caused by moisture on the cell contacts, and it is therefore thought likely that moisture was also responsible for the high readings in 1976. The presence of metal in both solution and sediments from the mine dumps had no effect upon the stream water conductivity. The small right bank tributary at locality 80, which flows entirely over the Pliocene Bovey Beds, had high conductivity, and a slight increase in conductivity in the Yarner Stream was observed as it flows further over these deposits.

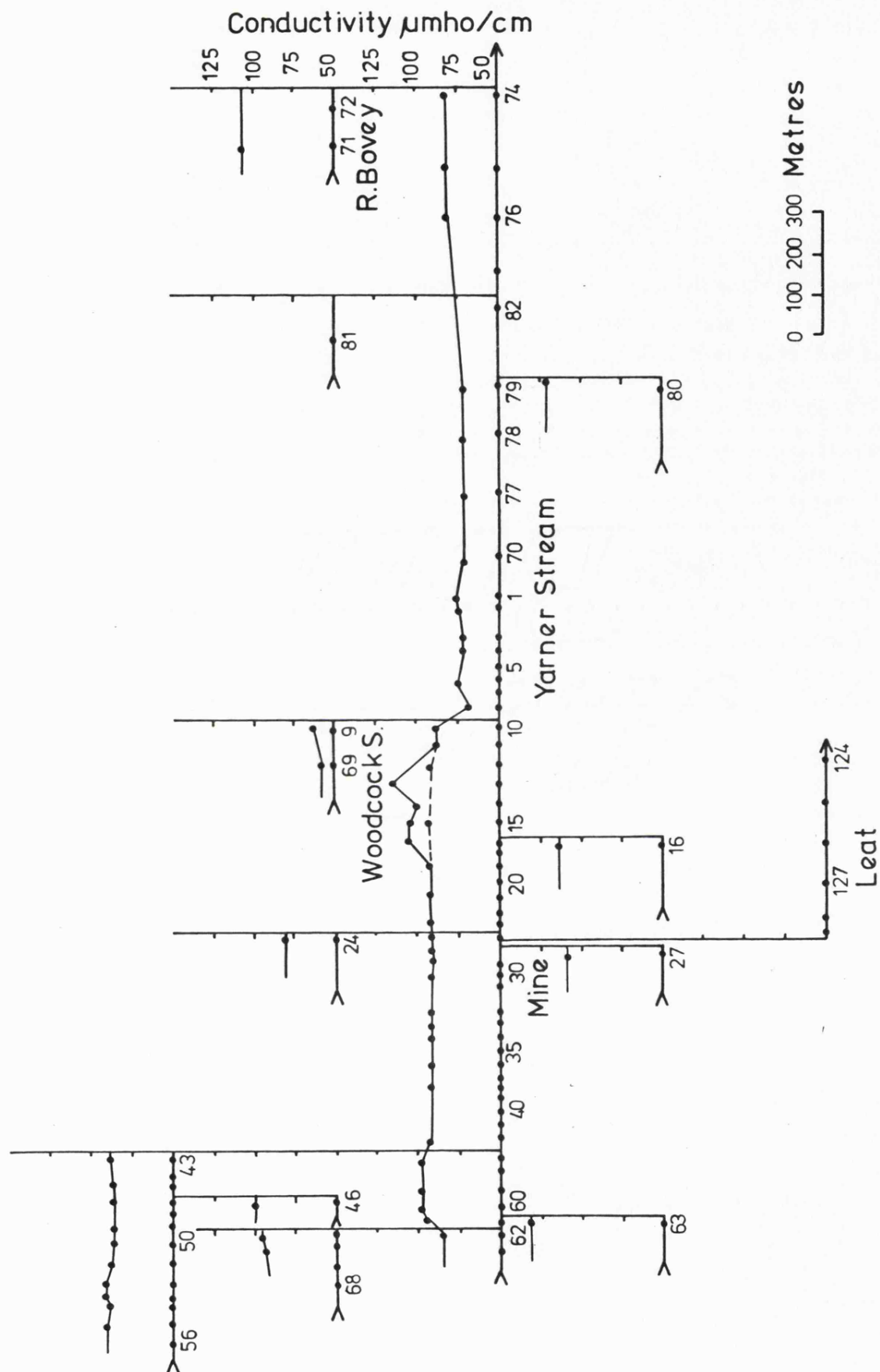


FIG. 8.12 SCHEMATIC PLOT OF STANDARDISED CONDUCTIVITY VALUES FROM YARNER WOOD

Measured April 1976 — — — Repeat in April 1977

## 8.2.3.5. Dissolved oxygen content.

The dissolved oxygen content of the stream waters was measured at a number of localities. It was hoped that this parameter might prove to be a useful alternative to Eh, which is notoriously difficult to measure reliably. Whilst measurement was not difficult, it was somewhat time consuming, requiring about 15 minutes for the electrode to stabilize.

The dissolved oxygen content of the stream water, measured in situ at various sites on October 15th 1977, corrected for temperature and atmospheric pressure, ranged from 1.3 to 13.0 mg/L. The highest recorded values (shown in Table 8.4) were at localities 26, 33, 43 and 57. It is interesting to note that where very prominent Fe staining is present in the stream, as, for example, at locality 23 and again at 46 and 47, the dissolved oxygen content falls slightly. The most interesting feature of these data are shown by the results from localities 27 and 63, which are the sites of springs emerging from collapsed mine adits (see Plates 14 & 15). Five readings were made near locality 27 at various distances from the source of the spring. 27F was at the mouth itself, 27E was 50 cms away, 27D was 2m away, 27C was 4m away and 27A was 5m away, at the point where the spring water reaches the main stream. Thus, in the space of 5m, from the source to the main stream, the dissolved oxygen content of the water had risen from 1.3 mg/L to 10.0 mg/L, a value typical of the stream elsewhere. A similar rapid oxygenation was observed at locality 63.

Whilst there was a substantial range in dissolved oxygen contents in Yarner Stream, no obvious correlation exists between them and the Eh values measured on the same day (see Table 8.4), and considerably more work will be necessary in order to evaluate the usefulness or otherwise of dissolved oxygen content measurements.



PLATE 14

Spring flowing from collapsed adit at locality YW 27,  
Yarner Wood.



PLATE 15

Spring flowing from collapsed adit at locality YW 63,  
Yarner Wood.

**TABLE 8.4** Dissolved oxygen content and Eh of Yarner Stream on October 15th 1977

<u>Sample Locality</u>	<u>Temp. (°C)</u>	<u>Oxygen content</u> <u>(mg/L)</u>	<u>Eh</u> <u>(mv)</u>
9	12	9.6	150
10	11.5	9.7	250
12	12	10.1	210
14	11.5	10.6	230
16	12	10.4	210
17	12	9.8	230
19	12.5	10.4	170
23	13	8.5	155
26	12.5	11.8	220
27A	14	9.7	130
27C	13.5	10.0	135
27D	14	6.2	170
27E	14	4.9	180
27F	14	1.3	170
28	13	12.2	255
33	12	13.0	225
43	12	11.8	230
46	11	9.5	225
47	12	8.5	210
57	12	12.9	240
58	11	10.5	195
60	11	10.0	230
62	11	10.8	260
63A	10	4.7	190
63C	10.5	7.5	210
64	11	10.8	255
124	12.5	10.6	260
125	12	10.5	270
126	12	10.4	240
127	12	10.5	240
128	12	10.5	230

#### 8.2.4. Soil samples

The results of the stream sediment and water analyses given above, have led to the conclusion that metal, especially Cu, is added to the Yarner Stream near localities 17 and 10, as well as in the vicinity of the mine dumps themselves. Two traverses were laid out (see Fig. 8.13), and soil samples were collected from the B horizon every 25m along them. The results of analysis by AAS, of 0.5g of minus 125 micron material, for Cu,Pb,Zn,Fe,Mn,As,Cd,Co and Ni are shown in Table 8.5, and these results are shown graphically in Figs. 8.14 and 8.15. Analyses of samples of alluvial soils, collected at YWSL 9 and YWSL 34, were omitted from Figs. 8.14 and 8.15.

It can be seen from Fig. 8.14 that the Cu results appear to indicate mineralisation over some 200m of the central portion of the traverse. This same zone showed up as a broadly anomalous area in the data for Fe,As and, to a lesser extent, Ni, and, at a rather low absolute level, for Pb. Isolated high values from the Mn, Zn, and Co results imply a less widespread primary distribution for these elements than for Cu,Pb, Fe,As and Ni. There is an indication, especially from the Fe results, that further mineralisation may be encountered to the north west of Site YWSL 15.

Fig. 8.15, which displays the results from the more westerly traverse, shows that a zone, approximately 150m wide, gave rise to slightly anomalous Cu values and that high Pb,Fe and As values coincided within this zone. There is also an indication, from the Cu,Pb,Zn,Fe, As,Cd and Ni results, that further mineralisation may be encountered to the south east of Site YWSL 21. Some support for this idea comes from the description, by Dines (1956), of a shaft at approximately 27840780.



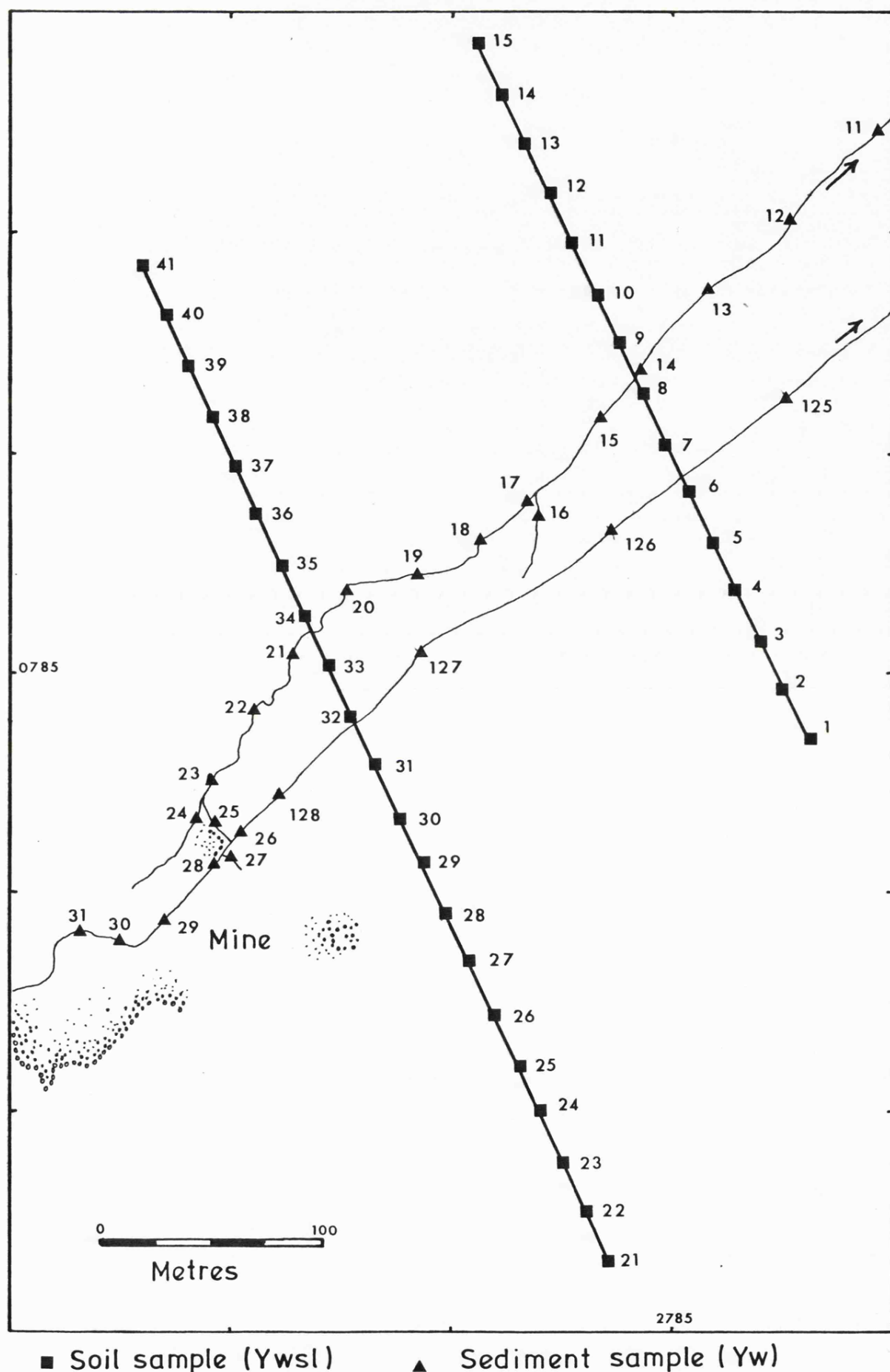


FIG. 8.13 MAP TO SHOW SOIL TRAVERSES IN YARNER WOOD



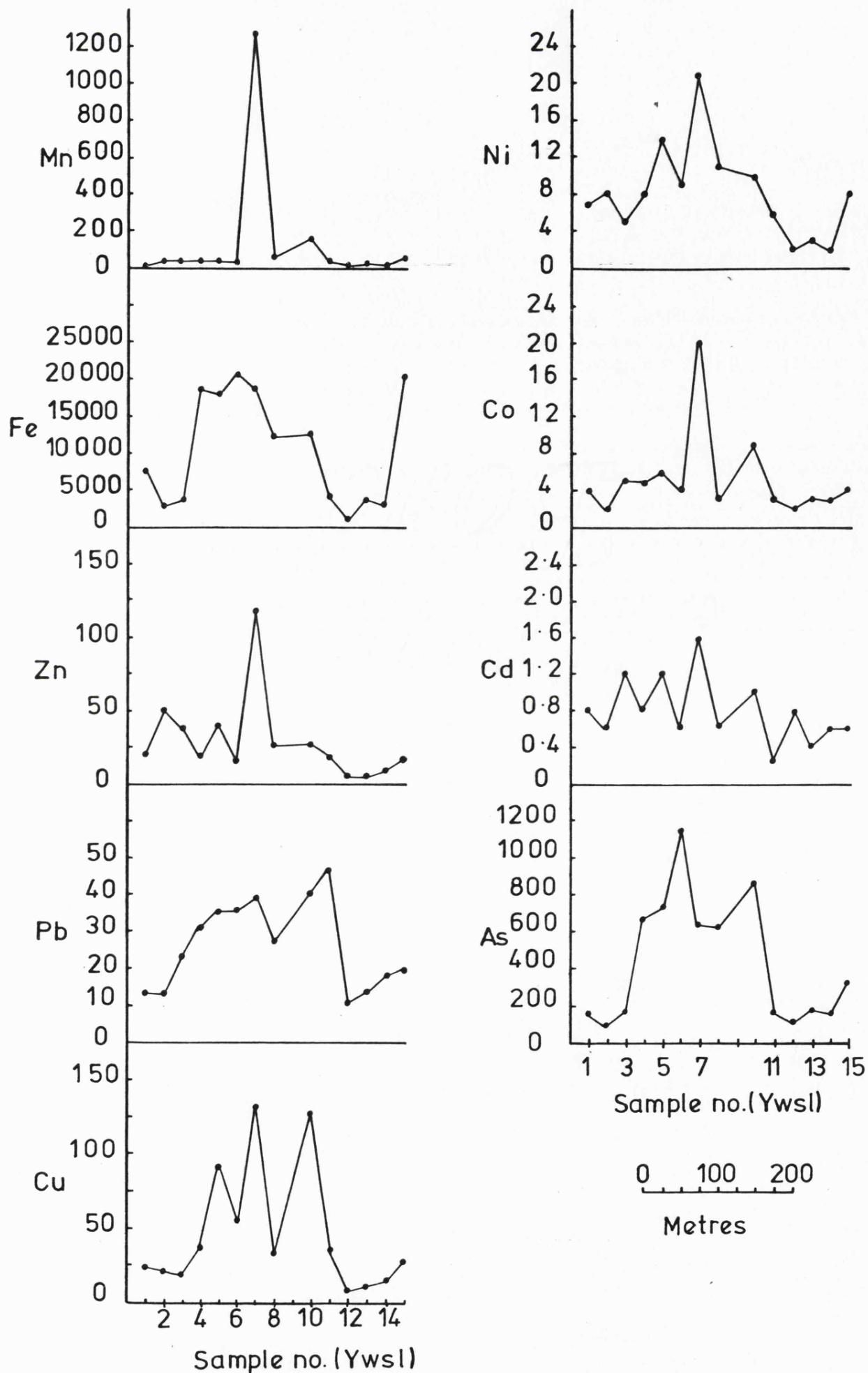


FIG. 8.14. METAL CONTENT OF RESIDUAL SOILS, Ywsl 1 - 8, 10 - 15, YARNER WOOD. ALL IN ppm

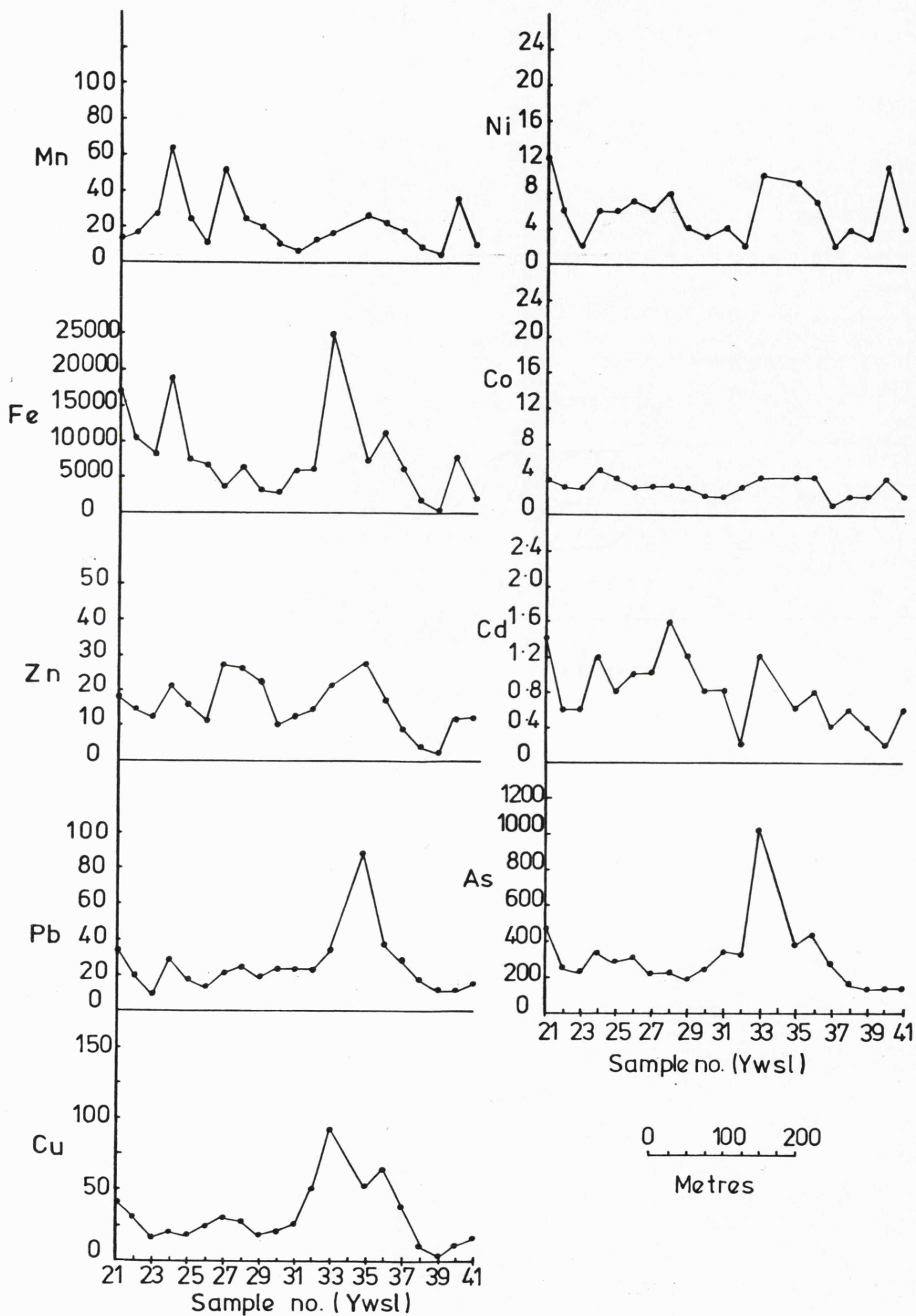


FIG. 8.15 METAL CONTENT OF RESIDUAL SOILS, Ywsl 21 -33, 35 -41. YARNER WOOD. ALL IN ppm.

TABLE 8.5

8.17

Analytical results, Yarner Wood soil samples.

ALL IN PPM

YARNER WOOD SOILS. 9 ELEMENTS.

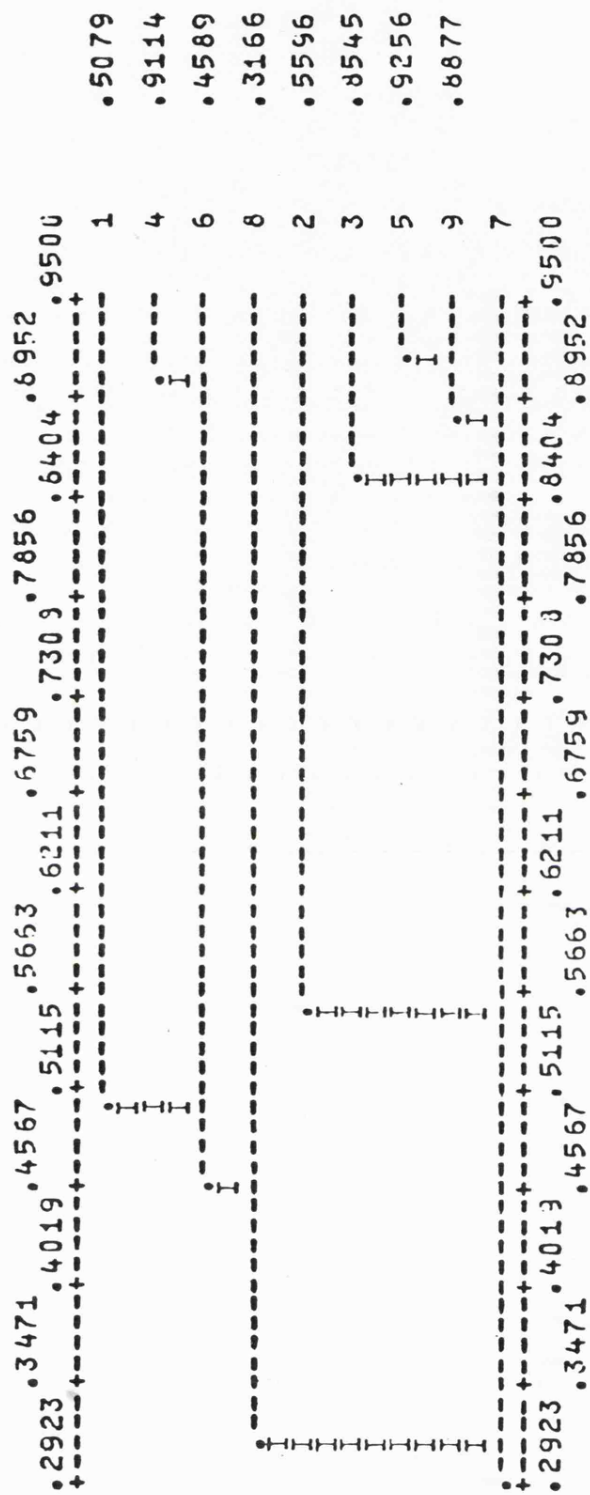
LOCALITY	CU	PB	ZN	FE	MN	AS	CD	CO	NI
1.	22.0	13.0	20.0	7500.0	10.0	160.0	.8	4.0	7.0
2.	21.0	13.0	50.0	2500.0	25.0	80.0	.6	2.0	8.0
3.	19.0	23.0	33.0	3500.0	34.0	160.0	1.2	5.0	5.0
4.	36.0	31.0	15.0	18400.0	30.0	600.0	.8	5.0	8.0
5.	31.0	35.0	34.0	17900.0	34.0	730.0	1.2	6.0	14.0
6.	55.0	35.0	15.0	20000.0	24.0	1160.0	.6	4.0	9.0
7.	132.0	39.0	117.0	13700.0	1280.0	620.0	1.6	20.0	21.0
8.	33.0	27.0	25.0	12000.0	52.0	620.0	.6	3.0	11.0
9.	470.0	25.0	150.0	14500.0	128.0	1430.0	1.2	14.0	39.0
10.	129.0	40.0	27.0	12600.0	156.0	860.0	1.0	9.0	10.0
11.	36.0	47.0	19.0	3900.0	24.0	160.0	.2	3.0	6.0
12.	8.0	10.0	5.0	800.0	4.0	100.0	.8	2.0	2.0
13.	11.0	13.0	6.0	3300.0	22.0	180.0	.4	3.0	3.0
14.	15.0	15.0	3.0	2800.0	14.0	150.0	.6	3.0	2.0
15.	27.0	19.0	13.0	20300.0	56.0	330.0	.6	4.0	8.0
21.	40.0	33.0	19.0	17000.0	32.0	440.0	1.4	4.0	12.0
22.	31.0	19.0	14.0	10600.0	16.0	240.0	.6	3.0	6.0
23.	15.0	6.0	12.0	5100.0	26.0	220.0	.6	3.0	2.0
24.	20.0	20.0	21.0	10700.0	64.0	330.0	1.2	5.0	6.0
25.	16.0	17.0	16.0	7300.0	24.0	200.0	.8	4.0	6.0
26.	24.0	12.0	11.0	6600.0	10.0	300.0	1.0	3.0	7.0
27.	29.0	21.0	27.0	3500.0	52.0	210.0	1.0	3.0	6.0
28.	27.0	24.0	26.0	6200.0	24.0	220.0	1.6	3.0	8.0
29.	18.0	16.0	22.0	3100.0	20.0	180.0	1.2	3.0	4.0
30.	20.0	23.0	10.0	2700.0	10.0	230.0	.8	2.0	3.0
31.	26.0	23.0	12.0	5900.0	6.0	340.0	.8	2.0	4.0
32.	51.0	23.0	14.0	5900.0	12.0	320.0	.2	3.0	2.0
33.	38.0	33.0	21.0	25200.0	16.0	1040.0	1.2	4.0	10.0
34.	495.0	39.0	191.0	7100.0	70.0	3000.0	2.2	6.0	20.0
35.	52.0	36.0	27.0	7200.0	26.0	370.0	.6	4.0	9.0
36.	64.0	37.0	17.0	11100.0	22.0	430.0	.6	4.0	7.0
37.	32.0	28.0	9.0	6000.0	18.0	270.0	.4	1.0	2.0
38.	3.0	17.0	4.0	1600.0	8.0	160.0	.6	2.0	4.0
39.	3.0	11.0	2.0	300.0	4.0	130.0	.4	2.0	3.0
40.	11.0	11.0	12.0	7900.0	36.0	130.0	.2	4.0	11.0
41.	15.0	15.0	12.0	2000.0	10.0	130.0	.6	2.0	4.0

#### 8.2.5. Cluster analysis

Mention was made elsewhere (Chapter 5, Section 5.3.3.3., p. 5.36) of the apparent close correlation between Fe and As in data from Yarner Wood and attention drawn in Chapter 4, Section 4.3.3.3 (p.4.16), to the widely reported correlation between Mn oxides and base metals in stream sediments. Some method of measuring the correlation between the various elements was therefore sought. Obial and James (1973) have applied the technique of Cluster Analysis to multi-element applied geochemical data, and this approach was chosen for application to the stream sediment data from the Yarner Wood area.

Obial and James (op. cit.) argue for the use of either the unweighted or weighted pair-group average methods of linking, following a logarithmic data transformation, and the use of the correlation rather than distance coefficient as a measure of similarity. Adoption of the WPGA linkage allowed the FORTRAN computer program, given by Davis (1973, p. 467), to be readily adapted to accept a  $\log_{10}$  transformation. The adapted program is shown in Appendix 5.

R-mode cluster analysis considered the results for nine elements from 88 samples (one from each locality) as given in Appendix 4 and a dendrogram (Fig. 8.16) summarises the results. Obial and James (op.cit. Fig. 7) show a dendrogram drawn from the cluster analysis of a 50 x 20 matrix of random numbers. Less than 5% of the clusters occur above a correlation coefficient of 0.6, and so this level of similarity was chosen to discriminate groups within the present study. One group combines Fe and As, another combines Zn, Mn Ni and Cd, whilst Cu, Pb and Co remain ungrouped at  $r = 0.6$ . The very close correlation between Fe and As ( $r = 0.91$ ) strongly supports the idea, suggested in Section 5.3.3.3. (p.5.36), that As is present in



DENDROGRAM - VALUES ALONG X-AXIS ARE SIMILARITIES

Key:- 1=Cu, 2=Pb, 3=Zn, 4=Fe, 5=Mn, 6=As, 7=Cd, 8=Co, 9=Ni.

Fig. 8.16. Dendrogram of R-mode cluster analysis (WPGA),  
88 samples from Yarner Wood area, 9 elements.

the area as ferric arsenate, in association with ferric hydroxide. The other group of elements, Mn,Zn,Cd and Ni, are also closely correlated (Mn to Ni  $r = 0.93$ , Mn to Cd  $r = 0.89$ , Mn to Zn  $r = 0.85$ ). This strongly supports the theory of co-precipitation of metals with manganese oxides in this particular stream, but it is interesting to note that Cu, Co and Pb are not associated with Mn coatings on the sediments.

Q-mode cluster analysis was achieved on the same matrix of data by transposition, and the localities which formed clusters, with  $r = 0.45$ , are shown in Table 8.6. The dendrogram is shown in Fig. 8.17.

**TABLE 8.6** Localities which form clusters after Q-mode cluster analysis,  $r = 0.45$ . Yarner Wood area stream sediments. 9 elements, 88 localities

<u>Cluster</u>	<u>Localities</u>
A	1,2,3,4,5,6,7,8,10,11,12.
B	13,14,16,17,18,19,22,23,24,25,55,58,81,83,124,125,126,128.
C	15,20.
D	9,26,27,28,29,30,31,32,36,38,39,56,57,59,60,61,75,82.
E	33,34,62,63,64,65,66,76,78,79,80.
F	49,52.
G	21,37,40,41,43,44,45,46,47,48,50,51,53,54,67,68,69,70,71,72,73,74,77.
H	35,42,127.

Clusters A,B and C relate to the area around and up to 1 km downstream of the mine and demonstrate quite clearly that the association of elements related to the Cu mineralisation is well defined, and not present upstream of the mine, despite the numerous trial prospects into the hillside between localities 28 and 64. Indeed, it is interesting

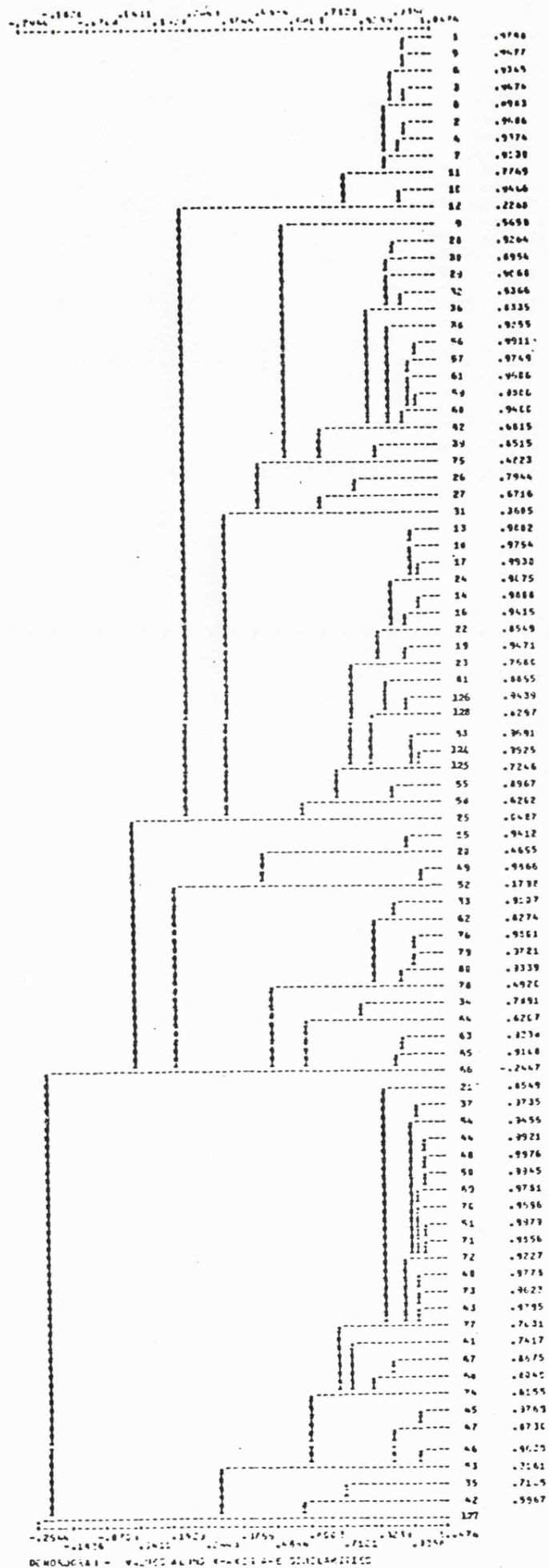


Fig. 8.17. Dendrogram of Q-mode cluster analysis (WPGA)

88 localities from Yarner Wood area, 9 elements.

to note that all evidence of old mine workings is upstream of the main shaft at 27830784. There are seven collapsed adit entrances between the old mine buildings and the headwater confluence at 27770783, but none downstream of the buildings. It therefore seems possible that the old miners, intent on exploration upstream of the mine, may have missed further mineralisation downstream.

### 8.3 CONCLUSIONS

Detailed sediment sampling in the Yarner Wood area was carried out in order to make an assessment of sources of imprecision. Subsequently, the results were interpreted in the context of the mineralisation in the region. AAS analysis, of the stream sediment samples for Cu, Pb, Zn, Fe, Mn, As, Cd, Co and Ni followed a hot 4M  $\text{HNO}_3$  digestion, and analysis of selected samples for Cu, Pb, Zn, Fe, Mn, Cd, Co and Ni followed a cold extraction digestion. Water samples, collected at certain localities, were analysed for Cu, Pb, Zn, Fe, Mn, As, Co and Ni by AAS, and sampling of the B soil horizon was carried out on two traverses which appeared to be substantially perpendicular to the strike of mineralisation. These soil samples were analysed for Cu, Pb, Zn, Fe, Mn, As, Cd, Co and Ni by AAS following a hot 4M  $\text{HNO}_3$  digestion.

A technique was devised which permits the graphical representation of metal content in stream sediments in two dimensions. This technique involves offsetting tributaries away from the plot of the main stream, and straightening out the bends in the streams.

The stream sediment results, plotted in this fashion, show that large amounts of Cu are added to the stream by the mine dumps, and further additions, possibly related to mineralisation, occur downstream around localities 17 and 10, and also around locality 127 in the artificial Leat distributary channel. The highest Pb values



occur in the headwater streams which drain the south west of the area, from Yarner Farm. A steady decrease in Pb values occurs downstream to the River Bovey. The spring at locality 63, emerging from a collapsed adit, is the source of a major metal anomaly, contributing large quantities of Zn, Fe, Mn, As, and Ni, and lesser amounts of Cd and Co. The way in which this anomaly is reduced for Zn and Mn is interesting because values for both metals above the mine are higher, by a factor of more than 2, than below the mine, with the exception of values for sediment from a stagnant pool at locality 25. The high Fe and As contents, caused by locality 63, are progressively diluted downstream as far as locality 30, where significant quantities of both metals are added to the stream both by the mine dumps, and by the mineralisation believed to be responsible for the Cu anomalies below the mine site. Significant increases in sampling error were detected in the portion of the stream where substantial ferric hydroxide precipitation occurs. (Section 3.3.2., p. 3.14). This increase, probably brought about by an inadequate separation of the Fe rich precipitate from the bed load sand-silt during sample collection, may be responsible for the somewhat erratic distribution of Fe between localities 1 and 10. The Cd and Ni contents of the sediments follow distribution patterns similar to those of Mn and Zn. Erratic Co contents between localities 30 and 10 appear to reflect the presence of mine dumps and postulated mineralisation, but the high values upstream of locality 50 and at locality 78 are problematical, though the former may be pH controlled, (see Fig. 8.11).

All the metals, except Pb, illustrate the distinct contrast between Yarner Stream and the River Bovey at their confluence. The results for Cu, Fe and As also clearly demonstrate a measure of dilution caused as the stream flows off the Carboniferous slates, and onto the Pliocene Bovey Beds.

In general, the cold extraction results show similar trends to those obtained by 'hot' extraction. Furthermore, the enhanced contrast obtained by cold extraction compared with the 'hot' attack, appears to be adequate to warrant the extensive use of the partial extraction technique in follow-up studies.

Improvements in AAS analytical capability, particularly with the use of flameless atomisation techniques, has permitted the detection of very small quantities of metal in acidified water samples. The resultant patterns are interesting for a number of reasons. Firstly, they reflect the patterns of mineralisation deduced from the sediment as, for example, at localities 10 and 17, where the results for Cu in the waters show pronouncedly high values. Similarly, high Pb values, at localities 58,60,62 and 64, reflect the anomalous Pb in the sediments from that area. Perhaps most significant, however, is the observation that the amounts of all 8 metals present in water sample 33 (assumed to be representative of the stream between localities 42 and 30 ) were very low indeed. This is in strong contrast with the sediment results for Zn,Mn,Co and Ni which showed higher values above the site of the mine than below it. This emphasises, rather forcefully, that the metal content of the system is in balance, with certain metals being confined to sediments in insoluble form in certain areas, and present in solution, with correspondingly lower sediment contents elsewhere. Thus, any

detailed understanding of the secondary environment should include collection of water samples as well as sediments. Additionally, water collection can be seen to be useful as a means of rapid follow-up sampling in mineralised areas.

Measurement of the pH of the stream waters revealed that above the site of the mine the stream had a pH very close to neutral, but that, once influenced by the mine dumps, the pH fell, reaching a minimum of 5.9. This may be the reason for the change in metal partition between sediments and waters, since Mn, for example, was shown by Hem (1972, Fig. 6) to be more soluble at pH = 6 than at pH = 7, by a factor of about 50. The sorption of metals such as Zn, Cd, Co and Ni by freshly precipitated Mn oxides and hydroxides is widely documented (see for example Anderson et al. (1973)) and it is therefore reasonable to suppose that Mn solubility will at least partially control the partition between sediment and water of such elements. Similar considerations probably also explain the low Fe content of the water from this locality, whilst the low Cu content probably reflects the fact that anomalous Cu is not present in the bed rock above the site of the mine anyway.

Measurement of the Eh, conductivity and dissolved oxygen content of the stream water was also carried out. It proved to be extremely difficult to obtain reproducible, reliable measurements of Eh, and further detailed consideration of this property will be necessary if significant results are to be obtained. Both conductivity and dissolved oxygen content proved to be fairly easy characteristics to measure, but of limited obvious significance, if the conclusion is correct that the conductivity anomaly detected between localities 17 and 14 in April 1976 was due to an instrument malfunction. It should be emphasised that this anomaly was not reproduced when re-measured the following year. It seems probable that the conductivity of

stream waters is more dependent on the quantities of major rather than minor or trace elements in solution. The most important feature of the dissolved oxygen results is the speed with which de-oxygenated water, issuing from the springs at localities 27 and 63, reached equilibrium with the atmosphere.

Soil sampling confirmed mineralisation which appears to have a trend sub-parallel to the Yarner Stream valley. The results imply that certain elements have a broader primary distribution pattern than others. Arsenic and Fe for example, appear to be particularly widely distributed as do Cu and Pb, although Pb values are low in absolute terms. Isolated peaks also occur within the Cu results, possibly pinpointing individual veins. The results for Zn, Mn, Co and Ni show some isolated high values whilst the Cd results are singularly inconclusive. There are some indications that further mineralisation may be encountered beyond the northern end of the eastern traverse and beyond the southern end of the western one, the latter being a region in which Dines (1956) reported mining activity. It is scarcely surprising to find that Cu anomalies may be detected in soils overlying known Cu-bearing mineralisation, but the broad patterns shown by the distribution of As and Fe is perhaps unexpected, and may have wider significance.

Some degree of multi-variant statistical interpretation was undertaken by means of cluster analysis. The close association between Fe and As was quantified at  $r = 0.91$ , and the close correlation between Mn, Zn, Cd and Ni was also demonstrated by the R-mode analysis. Q-mode analysis was used, and was particularly successful in picking out the secondary distribution trains associated with the mineralisation. In a geographically restricted, small scale survey such as this, the simpler, graphical techniques employed may be more useful, but in

larger-scale situations cluster analysis is undoubtedly a fairly simple, but potent, method of pattern detection.

## CHAPTER 9

### CONCLUSIONS AND RECOMMENDATIONS FOR FURTHER WORK

#### 9.1 ANALYTICAL TECHNIQUES

#### 9.2 SEDIMENT SAMPLING PROCEDURES

#### 9.3 SEDIMENT SAMPLE PREPARATION TECHNIQUES

#### 9.4 WATER, AS A SAMPLING MEDIUM

#### 9.5 SEASONAL VARIATIONS

#### 9.6 THE YARNER WOOD AREA

CHAPTER 9CONCLUSIONS AND RECOMMENDATIONS FOR FURTHER WORK9.1 ANALYTICAL TECHNIQUES

Atomic absorption spectrophotometry was used, as far as possible, in this study, because it is by far the most reproducible of the analytical methods available at Leicester. It is, also, possible to effect in excess of 1000 determinations per working day on prepared samples. This speed of operation begins to rival even the DR Spec., although Stanton (1976, p.52) suggests 3200 determinations per day as a maximum for DR Spec. analysis. However, the DR Spec. does not offer anything like the same degree of reproducibility.

Analysis by AAS requires the input of samples in a liquid form and investigation was performed to determine whether the conditions for digestion, commonly used in many academic and industrial institutions, could be bettered, with special reference to reproducibility. Differing strengths of various leaching agents were used at several temperatures, within the constraint that a hot water bath, rather than a hot air or sand bath, was used for heating. It was found that satisfactory results were obtained using 25% (4M)  $\text{HNO}_3$  at  $95^\circ\text{C}$  for 4 hours. It was sobering to note that, after the one hour digestion commonly applied elsewhere, the rate of metal extraction was still very rapid. The extra time taken certainly resulted in more reliable data, and, provided plenty of water baths are available, a "stock-pile" effect should ensure that adoption of this digestion technique does not unduly effect the daily throughput.

The size and quantity of particles chosen for analysis was considered next. It was found that certain elements, such as Cu, Pb, Zn, Fe and Mn, are concentrated in the finer size fractions of stream sediments. Thus, an optimum combination was sought which could balance:-

- (a) fine grained material with realistically sized field samples, and
- (b) large sub-samples with the convenience and speed of weighing, sieving and using test tubes for digestion.

A sample weight of 0.5g of minus 125 micron (120 mesh BSS) was found to fulfil the requirements most closely, and the bulk samples collected from 5 different localities were found to yield, on average, in excess of 2.5% minus 125 micron material. This implies that standard sample collection techniques need not be unduly altered, notwithstanding the conclusions on sampling to be drawn later in this Chapter.

A similar investigation was conducted for elements, such as Sn, which are usually dispersed clastically in the secondary environment. In the case of material from Site P (see Fig. 1.1), the optimum particle size fraction appeared to be the minus 190 micron (minus 80 mesh BSS) material. This may relate, in fact, to both the distance downstream from the source of the clastic grains (in this case of cassiterite) and the original grain size of the cassiterite within the mineralisation and may be an observation of only local significance. The optimum devised for such metals as Cu, Pb, Zn, Fe and Mn, may, on the other hand, have wider application than the present limited study because these elements are likely to be similarly dispersed in broadly similar climatic environments.

Separation of sample material into heavy and light mineral fractions was shown to be a possible advantage when dealing with Sn, although further work, currently being carried out at Leicester, is undoubtedly necessary. Such separation was shown, in the present study area, to be not worthwhile when considering such elements as Cu, Pb, Zn, Fe and Mn.

Careful monitoring and distribution of instrumental drift has allowed estimation of instrumental errors during AAS analysis. It was found that, unless the detection limit is approached, analytical variance was less than 20% of the total error variance.



The concept of "aging" of samples, stored prior to analysis, was investigated and it proved impossible to be certain that the limited differences that were observed were not due to differences in standard solutions used for calibration. Dilute standard solutions, for AAS calibration, are generally only made up in small volumes, and are therefore quickly used up during regular analysis and systematic variations in metal content were found not to occur during such time periods. Indeed, the day by day re-making of standard solutions, often recommended, may, in fact, add to rather than detract from non-reproducibility in a large batch of samples.

Sample leaches were decanted from the test tubes used for digestion, prior to analysis, in order to avoid the risk of solid residues being drawn into, and hence blocking, the nebulizer input tube of the spectrophotometer. It was shown that such samples, left even for a few hours, are subject to evaporation losses which introduce serious non-reproducibility. The use of air-tight lids for sample containers is, therefore, deemed essential even if only overnight storage is contemplated.

It was found that analysis, based upon different sample weights of the same sample, gave rise to different results, with higher concentrations being recorded from smaller sample weights. Partial neutralisation of the acid, used in digestion, was demonstrated, although it is not thought to be the main cause of the problem since, even after digesting 1.0g of sample, (the maximum weight considered), the resultant acid solution still had a pH of 0.185, which represents very strong acid. It was noted, however, that the discrepancy in results disappeared when samples were diluted to similar matrix concentrations. Therefore, various aspects of AAS interference were investigated.

Spectral interference was discounted, and background interference ruled out following studies with a deuterium arc background corrector. The problem has features which suggest that physical interferences may be responsible. However, no differences in solution specific gravity were

detected, and the differences in sample viscosity, which were observed by timing the rate of aspiration of various samples, were shown to be statistically insignificant. Nevertheless, differences were observed, and the statistical testing, at least in part, reflects the crudity of the experiment devised, and further investigation of the viscosity of such samples is recommended.

Chemical interferences were investigated by varying the burner head position on the instrument, by substituting the hotter nitrous oxide-acetylene for the air-acetylene flame, and by using 0.5% lanthanum chloride solution for dilution. Some marginal improvement was observed when the lanthanum chloride solution was added, and its use is felt to be good standard practice, adding only 0.7 pence per digestion to costs, at present prices.

Non-linear AAS responses were observed, above certain concentrations, when multi-element, synthetic samples were compared with single element standard solutions, despite the use of the electronic curvature correction facility. It is hoped that observation of this rather disturbing phenomenon will provide the basis for further, more detailed investigations.

Thus, care in this respect must be exercised in any systematic survey, and especially when dealing with anomalous samples which may require extra dilution and/or reduction in sample weight in order to come within the range of the AAS instrument in use.

AAS determination of As, using an electrodeless discharge lamp and an air-acetylene flame, following a 4M  $\text{HNO}_3$  digestion, can be shown to be quicker and more rigorous than fusion techniques. It is believed that the As is present in the form of ferric arsenate, associated with ferric hydroxide, precipitated on the stream bed. The widespread presence of ferric hydroxide in streams in temperate climates implies that As may be widely distributed in this form. Further work is necessary to establish the general applicability of this technique.

Spectral interference between the 327.4 nm Cu resonance line and the 328.1 nm Ag line, using an 0.7 nm slit width, and a multi-element, hollow cathode discharge lamp, was observed. This may be overcome provided care is exercised during the setting-up procedure.

Whilst Sn determination by AAS was shown to be possible using an air-acetylene flame following an ammonium iodide digestion, difficulties with the digestion were experienced, especially when the sample weight was varied. This was attributed to variable losses of tin iodide vapour from the open-ended test tubes used during digestion. A more detailed evaluation of this digestion technique is considered to be necessary in the light of these findings.

## 9.2 SEDIMENT SAMPLING PROCEDURES

A programme of duplicate sampling, sub-sampling and analysis allowed evaluation of error variances. It was shown that total error variance was many times smaller than total data variance, and then total error variance was partitioned into its component parts. For Cu, Pb, Zn, Fe, Mn, As, Co and Ni it was found that sampling error was dominant over sub-sampling and analytical errors, whereas for Cd, the close approach of the observed values to the detection limit, meant that analytical error dominated.

Comparison with the detailed study undertaken in Yarner Wood by Harrison (1974) showed that, whilst total data variability was comparable for the two studies, reductions were achieved during the present study in all forms of error variance which could be isolated. This means that the variations observed in the present data may be interpreted, in the context of mineralisation, with a great deal more confidence. This adequately demonstrates that extra trouble and time taken over sampling and general analytical procedures is worthwhile in the context of more significant overall results.

It was shown that a significant contributory factor towards sampling errors in Yarner Stream, is the presence of an iron-rich, jelly-like precipitate covering the bed of the stream below the mine site. This Fe-rich material, which is generally higher in most of the base metals than the sand-silt bed load at the same localities, is, nonetheless, a part of the sediment load of the system, and its deliberate exclusion from samples, in fact, leads to the introduction of sampling bias. A problem, to which further work might usefully be applied, is, therefore, to determine the extent, if any, to which such material should be included in sediment samples.

The results of an experiment, designed to determine how many "grabs" of sediment may be considered representative of a stream at any particular locality, were probably seriously affected by the observation, determined independently, that the metal contents of sediment do not remain constant as the depth of sampling below the water-sediment interface is varied. Such changes have been observed previously (Plant, 1971) and attributed to variations in Eh and/or pH. The present findings are in at least partial conflict with those of Plant (op. cit.) and it is probably advisable, until further detailed work has been carried out, to restrict sample collection to the sediment-water interface. Indeed, in many headwater streams this may be the only available source of material.

An experiment, designed to investigate the presence or otherwise of variable sampling precision (as defined by Miesch, 1971), showed it to be largely absent for Cu, Pb, Zn, Fe and Mn in samples collected in the River Mardle, near Brookwood (see Fig. 1.3 for localities).

### 9.3 SEDIMENT SAMPLE PREPARATION TECHNIQUES

Intuition, tradition and the "rule of thumb", rather than experimentation, are some of the factors which control selection of techniques during sample preparation. It was shown, during the present study, that a significant degree of non-reproducibility may be introduced unless samples are dried very soon after collection, and this desire for speed prompted an investigation of various, elevated drying temperatures. Significant loss of reproducibility occurs at a temperature of 150°C, whilst, at 500°C, it appears that substantial changes in clay mineralogy have taken place, causing considerable changes in the sample chemistry. Furthermore, the paper sample bags, commonly used, become brittle at about 150°C, thus setting a further upper limit to drying temperature from the point of view of convenience. Further detailed investigations, within the temperature range 70-150°C, would, undoubtedly, prove interesting.

In an attempt to avoid the introduction of any variable bias during sample preparation, mechanical devices were used for both sample sieving and sample splitting. A slight bias within the splitting machine was detected and a method of eliminating it devised.

The need for a systematic, standardised sieving process was highlighted by the findings of an experiment, designed to investigate possible variations in sample chemistry at various times after the commencement of sieving. It was found that the metal content of the samples investigated, from Yarner Wood, increased with sieving time, at least up to 60 seconds. This was believed to be related to the presence of metal-rich Fe and /or Mn oxide-hydroxide coatings.

Similar trends were present in only one of five samples collected in the Brookwood area where such coatings are largely absent. If abrasion, within the sieve, of oxide-hydroxide coatings is responsible for this feature, a light grinding, prior to sieving, may liberate the coatings and lead to better reproducibility. Further work might well investigate this possibility.

An attempt to homogenise sieved sample material, prior to sub-sampling, was made by adopting a technique which entails emptying the entire packet of material onto a sheet of paper, and sub-sampling from one quarter of the resultant cone. It is felt that this process, albeit slightly more lengthy than scooping material directly from inside the sample packet, may be better standard practice, especially if, as commonly happens, samples have been air-freighted prior to analysis. Additional studies into this aspect of the present work, might be directed towards some investigation of in-flight settling in sample material.

#### 9.4 WATER AS A SAMPLING MEDIUM

The existence of chemical and physico-chemical equilibria between sediment and water, (where present), in the drainage channel environment, means that any attempt at a complete understanding of metal dispersion in that environment must include analysis of, and physico-chemical measurements on, the stream water. Problems, associated with the detection of the minute quantities of metal commonly present in natural waters, have been largely solved by the introduction of flame-less atomisation techniques in AAS. However, flame atomised AAS is still preferable, where concentration levels make it possible, from the points of view of speed, convenience and cost.

Flame-less atomisation for AAS first became possible at Leicester in December 1977, and, whilst results obtained from the present study appear to be significant, substantial refinements of technique will undoubtedly be possible as more work is carried out using the apparatus.

A preliminary comparison of sampling and analytical errors for waters, has substantially confirmed the conclusion that water is a homogeneous sampling medium. However, some degree of sampling error was detected for Zn, and further investigation of this conclusion seems essential. Special attention should be paid to the mixing of streams or rivers below confluences.

Investigation of possible sources of contamination has revealed that the sealing pads inside the lids of the bottles used for water sample collection were a serious source of Zn contamination. Additionally, some batches of concentrated hydrochloric acid, used to acidify samples, were found to be sources of Fe contamination. Ultra-pure HCl was therefore used, despite its premium price.

Repeated analysis of water samples, over periods of up to two years, revealed that metal contents of the samples were unaffected by the presence or absence of chloroform in the sample container. Significant reductions with time in the Fe contents of all unacidified samples were recorded, whilst some, but not all, unacidified samples from the restricted field area of Yarner Wood, showed reductions, with time, in their Mn and Zn concentrations. No reductions in metal content were observed in acidified samples, indeed, slight increases in metal content were recorded for some samples. These may have been caused by contamination, or by metal being slowly leached from suspended, solid matter. If the latter is

the cause, filtration in the field might have to be contemplated. However, provided all steps are taken, short of filtration, to exclude solid material from the samples, and they are analysed as soon after collection as is convenient, the problem of increasing metal content may be at least minimised, if not overcome. Similarly, if the increases were brought about by progressive contamination from the sample containers, analysis as soon as possible after collection will also minimise the effect.

Certain of the problems, set by the need to acidify samples in the field, may be overcome if samples are acidified at the field headquarters at the end of each day. The introduction of bias, by this technique, has not been directly investigated, and further work in this area might include its consideration.

The lowering of detection limits, brought about by flame-less atomisation AAS techniques, may now enable water to be used as a regional reconnaissance sampling medium, as well as a follow-up medium. Indeed, the detection of significant variations in background concentrations of certain metals in waters may now be possible. Furthermore, water has some advantages over sediments, as a regional sampling medium, particularly in the respect that it appears to be largely free from sampling errors. Therefore, unskilled sampling crews may be employed to cover an area very quickly, with only minimal risk of introducing variable sampling bias.

## 9.5 SEASONAL VARIATIONS

The metal content of sediment samples, collected on a weekly basis, throughout a one year period, showed systematic variations, by a factor of about 1.5, which can be related to seasonal changes



in the climatic conditions. Both short-term results, such as might be influenced by excessive rainfall, and long-term trends, may be detected. High values for Cu,Zn,Mn,Cd,Co,Ni and Sn occurred in the winter months, whilst high values for Fe and As occurred in the summer. The Pb values recorded showed no long-term variations.

Water samples, collected on a similar basis, showed even more variation, ranging from a factor of 2.0 for Cu, to a factor of 4.7 for Fe. High values for Cu,Zn,Fe and Mn occurred in samples collected during the summer months. In all cases, for both sediments and waters, but especially the latter, the result shows a more erratic distribution in the winter than in the summer.

The antipathetic relationship between sediments and waters for Cu,Zn and Mn, and the sympathetic relationship for Fe, can be explained in terms of the relative importance of groundwater flow and surface run-off dilution, in feeding both the sediment and water supply of the stream. Precipitation of ferric hydroxide, directly from solution, is also seen as an important control over the Fe and As contents of the sediments.

The magnitude of variation observed in the sediments, for most elements, is in excess of that which can be explained purely by error variance, and is considered to be significant in the context of geochemical mapping, and possibly in the context of evaluation of subtle anomalies related to mineralisation. However, it is unlikely to affect the results of surveys designed to locate "sore thumb" anomalies.

If water is to achieve some degree of acceptance as a regional sampling medium within applied geochemistry, seasonal variations must be considered. Sampling at times of low run-off, (i.e. summer), seems to be advisable from two points of view:-

- (a) the minimising of rapid, seasonal fluctuations, and
- (b) because the samples contain higher absolute levels of metal.

Further investigation of seasonal variation in both sediments and waters seems to be justified. The present study was very limited in geographical scope, and further work might try and establish variations in other areas, both mineralised and background, with perhaps daily sampling where teams of samplers can be organised.

#### 9.6 THE YARNER WOOD AREA

The reduction of sources of error variation in geochemical data means that the remaining variance may be interpreted more confidently in the context of natural variability, and means, furthermore, that complicated, statistical smoothing techniques are less necessary. A simple plotting technique was devised and used to interpret the stream sediment data from Yarner Wood. The resultant patterns, supported by limited sediment cold extraction and water sample analysis, indicate that above background concentrations of Cu do not occur upstream of the old mine dumps, but that Cu, related to the old mine dumps and also possibly to sub-outcropping mineralisation, is added to the system between the mine and the confluence with the Woodcock Stream. Similar indications of mineralisation are demonstrated by the results for Fe, As and Co. A spring, issuing from a collapsed adit at locality 63, is the source of a prominent Zn, Fe, Mn, As, Cd, Co and Ni anomaly, whilst high Pb values have their source in the two headwater streams draining Yarner Farm. Lead is the only element not to show at least a two-fold contrast with the River Bovey at the confluence with Yarner Stream.

Cluster analysis provided useful information, the association of Fe with As and of Zn,Mn,Cd and Ni being detected by R-mode analysis, and the areas of high Cu values standing out particularly clearly from the results of the Q-mode analysis.

Soil sampling confirmed that the mineralisation appears to have a trend sub-parallel to the Yarner Stream valley. Whilst anomalies were detected for Cu, (hardly a surprising result), the widespread distribution of high As and Fe values was somewhat unexpected, and may be shown, by future work, to have considerably wider significance.

The partition of metals between sediments and water, and the control of such partition by physico-chemical factors, notably pH, was demonstrated in the section of the stream above the old mine. Here it can be shown that, at neutral pH, elements such as Mn,Zn,Cd,Co and Ni are relatively insoluble, and hence concentrated in the sediments, with low concentration in the stream water. Further downstream the pH falls, as acid waters enter from the mine waste heaps, and the partition of elements alters, with the sediments containing considerably lower levels of these metals while much more metal is carried in solution. This demonstrates the necessity of water sample analysis in any detailed evaluation of metal dispersion in the secondary environment.

The measurement of Eh in natural waters proved to be particularly difficult, and the use of the waters' dissolved oxygen contents was considered as an alternative. Whilst spectacular oxygenation of water issuing from springs was noted, any confirmation

of a possible working relationship, between Eh and dissolved oxygen content, awaits much more detailed work.

Measurements of stream water conductivity appear to be dominated by major elements in solution, and influxes of trace metal, associated with mineralisation, do not appear to have been detected.

Further detailed sampling of the Yarner Wood area might well be considered in the light of the soil sampling results, which demonstrated the usefulness of Fe and As, as well as Cu, as pathfinder elements. The indications of further mineralisation beyond the northern limit of the more easterly traverse and beyond the southern limit of the more westerly traverse are encouraging. Further work might also try to locate the source of the metals entering the system via the collapsed adit at locality 63, as well as locating the source of lead coming from the Yarner Farm area.

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## APPENDICES

- Appendix 1      Computer programme TOMHOW, for computing precision, and specimen printout.
- Appendix 2      Computer programme LANVA2, for 2-way analysis of variance computation, and specimen printout.
- Appendix 3      Analytical results 152 stream sediment samples, Yarner Wood.
- Appendix 4      Analytical results, one stream sediment sample from each of 88 localities in Yarner Wood.
- Appendix 5      Computer programme CLUSTR, and the necessary sub-routines READM, PRINTM, LOGTRN, STAND, RCOEF, DIST, WPGA, DENDRO.

# APPENDIX 1

```

PROGRAM TOMHOW(INPUT,OUTPUT,TAPE5=INPUT,TAPE6=OUTPUT)
DIMENSION PPM(100,10),ALGPPM(100,10)
DIMENSION PPMN(100),ALGMN(100),PE(100)
DO 900 I=1,N
DO 910 J=1,M
PPM(I,J)=0.0
ALGPPM(I,J)=0.0
910 CONTINUE
900 CONTINUE
DO 920 I=1,N
PPMN(I)=0.0
ALGMN(I)=0.0
PE(I)=0.0
920 CONTINUE

CC
CC READ IN VALUES OF N AND M FOR I AND J RESPECTIVELY
CC
CC READ(5,1000)N,M
CC
CC READ MATRIX PPM(I,J), CONVERT TO LOG10, FIND MEANS FOR EACH I VALUE
CC
DO 100 I=1,N
READ(5,3000)(PPM(I,J),J=1,M)
SUM=0.0
DO 110 J=1,M
ALGPPM(I,J)=ALOG10(PPM(I,J))
SUM=SUM+PPM(I,J)
110 CONTINUE
PPIMN(I)=SUM/FLOAT(M)
SUMA=0.0
DO 120 J=1,M
SUMA=SUMA+ALGPPM(I,J)
120 CONTINUE
ALGMN(I)=SUMA/FLOAT(M)
100 CONTINUE

CC
CC CALCULATE THE  $T=M*(M-1)/2$  PRECISION ESTIMATORS FOR EACH VALUE OF I,
CC SUM, AND DIVIDE BY T, GIVING ONE ESTIMATOR, PE, FOR EACH I
CC
DO 200 I=1,N
SUMPRE=0.0
K=M-1
DO 300 J=1,K
ICOUNT=1
10 IF(J+ICOUNT.GT.M)GO TO 20
DIFF=ABS(ALGPPM(I,J)-ALGPPM(I,J+ICOUNT))
SUM=ALGPPM(I,J)+ALGPPM(I,J+ICOUNT)
PRE=400.0*DIFF/SUM
SUMPRE=SUMPRE+PRE
ICOUNT=ICOUNT+1
GO TO 10
20 CONTINUE
300 CONTINUE
T=K*(K-1)/2
PE(I)=SUMPRE/T
200 CONTINUE
WRITE(6,2000)
WRITE(6,3000)
DO 500 I=1,N
WRITE(6,3500)(PPM(I,J),J=1,M)
WRITE(6,3750)PPMN(I)
WRITE(6,4000)(ALGPPM(I,J),J=1,M)
WRITE(6,4250)ALGMN(I)
WRITE(6,4500)PE(I)
500 CONTINUE
WRITE(6,2000)
WRITE(6,5000)
WRITE(6,5000)(PE(I),I=1,N)
1000 FORMAT(2(I4,2X))
2000 FORMAT(1H1,5X,*SITE G -24+90 HEAVIES TBE CU,PB,ZN,FE,MN*)
2500 FORMAT(1H1,10X,*MEANS*,10X,*TOMHOW PREC*,//)
3000 FORMAT(10(F5.0,2X))
3500 FORMAT(2X,10(F6.3,2X))
3750 FORMAT(1H+,10X,F6.3)
4000 FORMAT(2X,10(F6.4,2X))
4250 FORMAT(1H+,10X,F6.4)
4500 FORMAT(1H+,10X,F4.1,/)
5000 FORMAT(5X,*TOMHOW PRECISION ESTIMATES FOR EACH I*,//)
6000 FORMAT(5(4X,F4.1),/)
STOP
END

```

APPENDIX 1 continued over ...

# APPENDIX 1 continued

SITE G -24+80 HEAVIES TBE CU,P,ZN,FE,MN					MEANS	TOMHOW PREC
410. 2.6128	710. 2.8513	370. 2.5682	430. 2.6335	550. 2.7404	494. 2.6812	10.3
670. 2.8261	555. 2.8162	445. 2.6484	360. 2.9345	1230. 3.1072	782. 2.6665	14.4
487. 2.6875	567. 2.7686	550. 2.7404	762. 2.8820	725. 2.1603	622. 2.7878	7.3
625. 2.7959	475. 2.5767	604. 2.7839	450. 2.6532	533. 2.6344	568. 2.7488	7.0
900. 2.9542	525. 2.7359	510. 2.7076	610. 2.7353	470. 2.6721	623. 2.7530	9.3
3500. 3.5441	5500. 3.7404	3900. 3.5311	3700. 3.5682	5200. 3.7150	4360. 3.6319	5.9
5150. 3.7116	5350. 3.7672	7600. 3.8503	6350. 3.8028	5300. 3.7709	6170. 3.7667	3.9
4500. 3.6532	5500. 3.7404	4250. 3.6234	3525. 3.5593	4250. 3.6284	4425. 3.6419	4.2
3417. 3.5336	4000. 3.4021	4750. 3.6759	4250. 3.6234	4417. 3.6451	4167. 3.6172	3.7
3650. 3.5623	3350. 3.5855	4200. 3.6232	4100. 3.6128	4050. 3.6075	3970. 3.5982	1.7
570. 2.7559	800. 2.8031	1850. 3.2742	630. 2.7933	420. 2.6232	860. 2.8711	19.6
1075. 3.0314	1150. 3.0607	645. 2.8036	1300. 3.1139	370. 2.3335	1008. 2.9910	9.8
987. 2.9343	525. 2.7959	1225. 3.0107	312. 2.9600	537. 2.3041	837. 2.9130	8.5
833. 2.9206	333. 2.9206	517. 2.7135	553. 2.7456	1534. 3.1998	865. 2.9002	15.6
765. 2.8837	715. 2.8543	375. 2.9420	655. 2.8162	375. 2.8420	777. 2.8876	4.7
4400. 4.6435	5400. 4.7324	5050. 4.7533	4700. 4.6721	5150. 4.7113	4940. 4.6926	1.9
3700. 4.5682	3750. 4.6711	3925. 4.5038	4000. 4.6021	4700. 4.6721	40100. 4.6015	2.1
5100. 4.7076	5000. 4.6930	5350. 4.7284	5000. 4.6930	4700. 4.6721	50300. 4.7012	1.8
48357. 4.6245	45122. 4.5534	46500. 4.5592	45500. 4.6593	34350. 4.7353	48024. 4.6804	1.6
49600. 4.6355	45000. 4.5590	47600. 4.6776	48000. 4.6812	30400. 4.7024	48240. 4.6831	.9
900. 2.9542	1725. 3.2355	320. 2.3538	320. 2.7138	1120. 3.0492	1096. 3.0233	9.6
990. 2.9356	150. 2.9542	700. 2.8375	149. 3.1732	1270. 3.1238	1088. 3.0249	9.2
890. 2.9494	375. 2.9630	1245. 3.1111	1162. 3.0652	1125. 3.0512	1039. 3.0148	3.9
975. 2.9690	350. 2.9777	133. 2.9296	592. 2.9491	1300. 3.0000	890. 2.9455	5.3
885. 2.9459	821. 2.9138	323. 2.9538	320. 2.9638	315. 2.9112	872. 2.9399	2.1

SITE G -24+50 HEAVIES TBE CU,P,ZN,FE,MN  
TOMHOW PRECISION ESTIMATES FOR EACH I

10.3	14.4	7.3	7.0	3.3
5.9	3.9	4.2	3.7	1.7
13.8	9.8	9.5	15.6	4.7
1.9	2.1	1.0	1.6	.9
3.6	3.2	3.9	5.3	2.1

## APPENDIX 2

### DIFFERENCES IN TREATMENT MEANS

SOURCE OF VARIATION	SUM OF SQUARES	DEGREES OF FREEDOM	MEAN SQUARES	F-TESTS
AMONG SAMPLES	3.515643	19	.027139	
AMONG TREATMENTS	4.839378	12	.403262	1.180521
ERROR	5.241512	228	.022969	17.542302
TOTAL VARIATION	13.596533	259		

# APPENDIX 3

YARNER WOOD DATA FOR ALL SAMPLES, 9 ELEMENTS

ALL VALUES IN PPM.

	Cu	Pb	Zn	Fe	Mn	As	Cd	Co	Ni
YW 1a	330.0	32.0	90.0	52000.0	490.0	2200.0	2.0	38.0	23.0
YW 1b	325.0	31.0	100.0	46000.0	540.0	2500.0	2.0	47.0	29.0
YW 2a	340.0	34.0	120.0	82000.0	630.0	2820.0	1.5	60.0	33.0
YW 2b *	335.0	29.0	122.0	66000.0	150.0	3600.0	1.5	32.0	39.0
YW 3a	230.0	37.0	100.0	53000.0	340.0	3080.0	1.5	33.0	27.0
YW 3b *	160.0	29.0	34.0	130000.0	1380.0	7100.0	1.5	107.0	19.0
YW 4a	405.0	37.0	108.0	67000.0	840.0	2680.0	1.5	67.0	27.0
YW 4b *	540.0	37.0	66.0	131000.0	300.0	7500.0	1.5	36.0	29.0
YW 5a	520.0	37.0	100.0	69000.0	680.0	2900.0	2.0	53.0	30.0
YW 5b *	740.0	23.0	120.0	169000.0	410.0	9400.0	3.0	47.0	35.0
YW 5c	465.0	35.0	164.0	82000.0	490.0	3280.0	2.0	45.0	36.0
YW 6a	490.0	39.0	124.0	97000.0	550.0	4220.0	2.0	55.0	35.0
YW 6b	330.0	30.0	96.0	44000.0	174.0	2140.0	1.5	27.0	25.0
YW 6c *	40.0	16.0	16.0	420000.0	60.0	7500.0	2.0	24.0	34.0
YW 7a	410.0	38.0	80.0	53000.0	500.0	2780.0	1.0	41.0	26.0
YW 7b	285.0	35.0	132.0	43000.0	6200.0	2760.0	1.5	42.0	30.0
YW 8a	310.0	37.0	68.0	45000.0	170.0	2340.0	1.5	31.0	24.0
YW 8b	430.0	38.0	76.0	55000.0	430.0	3940.0	2.0	36.0	27.0
YW 9a	191.0	54.0	102.0	24000.0	184.0	680.0	1.0	25.0	23.0
YW 9b	181.0	46.0	112.0	21000.0	134.0	560.0	1.5	21.0	25.0
YW 10a	870.0	50.0	156.0	66000.0	2030.0	3980.0	3.0	142.0	51.0
YW 10b *	985.0	37.0	206.0	156000.0	540.0	10300.0	3.0	64.0	40.0
YW 11a	635.0	48.0	224.0	59000.0	740.0	3940.0	2.0	70.0	41.0
YW 11b	555.0	49.0	166.0	52000.0	2100.0	3280.0	2.5	115.0	46.0
YW 11c *	800.0	41.0	178.0	153000.0	1080.0	10900.0	2.5	98.0	38.0
YW 12a	535.0	42.0	166.0	52000.0	1200.0	3220.0	3.0	82.0	52.0
YW 12b	505.0	46.0	152.0	53000.0	1500.0	2960.0	3.0	86.0	55.0
YW 13a	455.0	41.0	172.0	52000.0	800.0	3040.0	2.5	35.0	43.0
YW 13b *	35.0	8.0	144.0	51000.0	30.0	23500.0	2.0	27.0	19.0
YW 14a	435.0	48.0	138.0	55000.0	1330.0	3600.0	2.5	89.0	51.0
YW 14b	425.0	44.0	172.0	44000.0	1210.0	2740.0	2.5	62.0	45.0
YW 15a	560.0	39.0	216.0	52000.0	450.0	6300.0	2.5	30.0	37.0
YW 15b	560.0	41.0	212.0	58000.0	530.0	5800.0	3.0	34.0	42.0
YW 15c *	3850.0	24.0	346.0	173000.0	3000.0	13100.0	5.5	183.0	67.0
YW 16a	400.0	50.0	260.0	59000.0	750.0	8200.0	5.0	84.0	48.0
YW 17a	710.0	49.0	260.0	54000.0	2100.0	3580.0	3.5	74.0	64.0
YW 17b	540.0	52.0	252.0	42000.0	1330.0	3460.0	2.5	56.0	58.0
YW 18a	535.0	50.0	240.0	61000.0	580.0	7000.0	2.5	46.0	50.0
YW 18b	815.0	49.0	146.0	81000.0	1200.0	8000.0	2.5	62.0	40.0
YW 19a	450.0	52.0	292.0	47000.0	1400.0	2460.0	4.0	61.0	78.0
YW 19b	455.0	46.0	250.0	41000.0	1470.0	2060.0	3.5	55.0	78.0
YW 19c *	430.0	28.0	340.0	96000.0	17200.0	3740.0	11.0	220.0	171.0
YW 20a	385.0	46.0	192.0	57000.0	1120.0	2240.0	3.0	43.0	54.0
YW 20b	450.0	43.0	142.0	50000.0	720.0	2120.0	2.5	35.0	46.0
YW 21a	555.0	64.0	304.0	49000.0	2900.0	2020.0	4.0	67.0	74.0
YW 21b	515.0	56.0	296.0	60000.0	3100.0	2480.0	3.5	70.0	75.0
YW 21c *	580.0	34.0	1400.0	127000.0	18600.0	6400.0	14.0	330.0	384.0
YW 22a	585.0	64.0	310.0	64000.0	3900.0	3000.0	4.5	83.0	96.0
YW 22b	520.0	67.0	282.0	54000.0	2900.0	2800.0	5.0	64.0	88.0
YW 22c *	725.0	34.0	1130.0	163000.0	11000.0	8700.0	11.5	210.0	217.0
YW 23a	660.0	68.0	520.0	68000.0	3700.0	3500.0	6.0	95.0	105.0
YW 24a	365.0	54.0	102.0	41000.0	710.0	1840.0	1.5	33.0	36.0
YW 24b *	220.0	21.0	352.0	370000.0	6600.0	12400.0	5.0	132.0	57.0
YW 25a	1005.0	85.0	1180.0	53000.0	7700.0	2240.0	10.5	146.0	196.0
YW 26a	335.0	60.0	212.0	45000.0	970.0	1880.0	2.0	32.0	41.0
YW 26b	430.0	57.0	262.0	60000.0	1600.0	2360.0	3.0	57.0	57.0
YW 27a	15.0	10.0	244.0	620000.0	260.0	10900.0	2.5	32.0	23.0
YW 27b	535.0	59.0	254.0	31000.0	1750.0	1360.0	4.0	42.0	67.0

APPENDIX 3 continued over ...



# APPENDIX 3 continued

YW 29a	300.0	51.0	172.0	26000.0	1300.0	1100.0	2.0	27.0	53.0
YW 29b	305.0	48.0	174.0	26000.0	1460.0	1060.0	3.0	30.0	55.0
YW 30a	810.0	83.0	206.0	39000.0	360.0	2100.0	3.0	17.0	43.0
YW 31a	350.0	74.0	540.0	39000.0	2300.0	1560.0	4.5	43.0	92.0
YW 31b	390.0	74.0	600.0	42000.0	4200.0	1800.0	5.0	69.0	113.0
YW 32a	175.0	79.0	530.0	47000.0	5300.0	2440.0	6.0	67.0	149.0
YW 32b	185.0	82.0	620.0	64000.0	5100.0	2300.0	5.0	75.0	158.0
YW 33a	154.0	76.0	655.0	42000.0	5600.0	2480.0	6.0	82.0	198.0
YW 33b	179.0	87.0	770.0	49000.0	7000.0	2320.0	6.0	80.0	190.0
YW 34a	135.0	70.0	560.0	36000.0	5000.0	2040.0	5.0	69.0	167.0
YW 34b	166.0	83.0	760.0	54000.0	7100.0	2520.0	7.0	93.0	202.0
YW 35a	144.0	70.0	565.0	42000.0	5400.0	2220.0	5.5	77.0	160.0
YW 36a	145.0	75.0	620.0	50000.0	6400.0	2580.0	6.0	78.0	173.0
YW 36b	135.0	70.0	620.0	44000.0	16100.0	2720.0	6.5	79.0	190.0
YW 37a	140.0	77.0	555.0	42000.0	4400.0	2360.0	5.5	71.0	156.0
YW 37b	130.0	75.0	440.0	33000.0	3400.0	1980.0	5.0	51.0	126.0
YW 38a	142.0	71.0	540.0	49000.0	5300.0	2920.0	5.5	84.0	161.0
YW 38b	149.0	69.0	550.0	52000.0	5200.0	2880.0	5.5	81.0	162.0
YW 39a	170.0	75.0	660.0	64000.0	7900.0	4240.0	6.0	90.0	154.0
YW 39b	160.0	76.0	600.0	51000.0	6000.0	3780.0	5.5	83.0	164.0
YW 40a	137.0	71.0	344.0	45000.0	5700.0	2940.0	5.0	76.0	138.0
YW 41a	185.0	64.0	520.0	54000.0	6800.0	3420.0	6.0	92.0	171.0
YW 41b	170.0	80.0	560.0	52000.0	7400.0	3220.0	5.5	89.0	176.0
YW 42a	190.0	78.0	720.0	49000.0	9600.0	2320.0	6.0	65.0	193.0
YW 42b	205.0	75.0	700.0	51000.0	19700.0	2160.0	6.0	70.0	191.0
YW 43a	85.0	33.0	66.0	16400.0	820.0	900.0	2.5	80.0	48.0
YW 43b	86.0	32.0	68.0	19800.0	830.0	960.0	2.5	79.0	49.0
YW 44a	80.0	32.0	52.0	23000.0	266.0	940.0	1.5	51.0	34.0
YW 45a	61.0	25.0	46.0	21800.0	480.0	1280.0	1.5	57.0	39.0
YW 45b	57.0	23.0	42.0	22000.0	340.0	1040.0	2.0	43.0	33.0
YW 46a	120.0	37.0	140.0	15500.0	1100.0	780.0	1.5	192.0	66.0
YW 47a	56.0	50.0	52.0	30000.0	220.0	1560.0	1.5	18.0	24.0
YW 47b	59.0	25.0	40.0	37000.0	280.0	1900.0	2.0	25.0	28.0
YW 48a	60.0	26.0	40.0	18400.0	230.0	1080.0	1.5	21.0	29.0
YW 48b	55.0	22.0	460.0	25000.0	320.0	780.0	1.5	24.0	29.0
YW 49a	70.0	34.0	36.0	26000.0	390.0	920.0	1.5	32.0	29.0
YW 49b	73.0	37.0	32.0	26000.0	370.0	980.0	1.5	35.0	30.0
YW 50a	50.0	17.0	26.0	2100.0	160.0	120.0	1.5	22.0	22.0
YW 50b	50.0	18.0	22.0	2200.0	130.0	80.0	1.5	20.0	27.0
YW 51a	125.0	31.0	74.0	7400.0	760.0	160.0	2.5	78.0	48.0
YW 52a	139.0	29.0	76.0	7400.0	860.0	120.0	3.5	100.0	42.0
YW 52b	157.0	29.0	86.0	6900.0	940.0	120.0	2.5	92.0	41.0
YW 53a	148.0	27.0	60.0	9100.0	310.0	220.0	2.5	99.0	46.0
YW 54a	135.0	31.0	36.0	8800.0	1100.0	200.0	4.0	109.0	55.0
YW 55a	145.0	45.0	44.0	11800.0	1640.0	560.0	2.0	178.0	35.0
YW 56a	162.0	40.0	42.0	8900.0	1270.0	160.0	2.5	126.0	35.0
YW 57a	152.0	83.0	855.0	57000.0	11200.0	2400.0	6.0	54.0	189.0
YW 57b	161.0	85.0	750.0	54000.0	9600.0	2240.0	6.0	48.0	179.0
YW 58a	140.0	95.0	840.0	53000.0	11700.0	2620.0	5.5	49.0	158.0
YW 58b	140.0	90.0	930.0	53000.0	11000.0	2940.0	5.5	51.0	172.0
YW 59a	144.0	93.0	1000.0	64000.0	14700.0	4400.0	7.5	71.0	227.0
YW 59b	145.0	84.0	1020.0	70000.0	17900.0	6200.0	8.0	83.0	240.0
YW 59c*	105.0	23.0	2820.0	190000.0	50000.0	15000.0	16.0	103.0	368.0
YW 60a	131.0	89.0	850.0	70000.0	15100.0	3480.0	6.0	52.0	136.0
YW 60b	135.0	85.0	960.0	65000.0	16700.0	3280.0	5.5	50.0	135.0
YW 61a	120.0	32.0	270.0	24000.0	920.0	400.0	3.0	19.0	60.0
YW 62a	130.0	31.0	306.0	15000.0	1010.0	520.0	3.5	23.0	78.0
YW 63a*	125.0	5.0	360.0	179000.0	18900.0	14300.0	5.0	93.0	200.0
YW 63b*	105.0	4.0	1400.0	135000.0	13000.0	11900.0	7.0	76.0	306.0
YW 64a	90.0	103.0	226.0	15300.0	690.0	200.0	2.0	12.0	33.0
YW 64b	100.0	110.0	244.0	14200.0	720.0	240.0	2.0	13.0	36.0
YW 65a	160.0	104.0	374.0	29000.0	2480.0	580.0	4.5	27.0	93.0
YW 66a	90.0	121.0	336.0	15200.0	1380.0	200.0	2.0	15.0	35.0
YW 67a	100.0	130.0	330.0	16200.0	790.0	260.0	2.0	15.0	38.0
YW 68a	100.0	140.0	302.0	16200.0	760.0	300.0	2.0	16.0	40.0

APPENDIX 3 continued over ...



# APPENDIX 3 continued

YW 69a	165.0	30.0	70.0	11800.0	450.0	440.0	2.0	42.0	21.0
YW 69b	165.0	30.0	72.0	12000.0	470.0	480.0	1.5	44.0	25.0
YW 70a	430.0	35.0	114.0	57000.0	830.0	2520.0	2.5	70.0	32.0
YW 70b	465.0	34.0	96.0	69000.0	840.0	2800.0	2.0	72.0	33.0
YW 71a	22.0	21.0	72.0	12800.0	390.0	60.0	1.0	9.0	13.0
YW 71b	19.0	19.0	64.0	12000.0	320.0	60.0	1.5	10.0	14.0
YW 72a	22.0	21.0	62.0	11700.0	270.0	80.0	1.5	8.0	11.0
YW 72b	22.0	20.0	66.0	11400.0	300.0	20.0	1.0	8.0	9.0
YW 73a	35.0	9.0	36.0	7300.0	90.0	60.0	1.0	7.0	19.0
YW 74a	225.0	24.0	162.0	22500.0	1010.0	760.0	3.0	81.0	47.0
YW 74b	235.0	23.0	144.0	22000.0	830.0	820.0	3.0	80.0	46.0
YW 75a	265.0	30.0	182.0	25000.0	760.0	820.0	3.0	71.0	44.0
YW 75b	250.0	26.0	148.0	24000.0	750.0	840.0	3.0	77.0	48.0
YW 76a	255.0	27.0	146.0	26400.0	680.0	900.0	2.5	66.0	46.0
YW 76b	230.0	26.0	138.0	27000.0	570.0	800.0	2.5	52.0	41.0
YW 77a	455.0	35.0	128.0	56000.0	1060.0	2080.0	2.5	87.0	37.0
YW 77b	420.0	33.0	110.0	52000.0	1100.0	2060.0	3.0	91.0	38.0
YW 78a	510.0	42.0	162.0	53000.0	1480.0	2340.0	3.5	124.0	52.0
YW 79a	395.0	35.0	108.0	41000.0	860.0	1600.0	2.5	63.0	36.0
YW 80a	54.0	20.0	80.0	9800.0	140.0	200.0	1.0	15.0	21.0
YW 81a	35.0	10.0	24.0	5300.0	10.0	80.0	1.0	4.0	10.0
YW 82a	285.0	29.0	120.0	28000.0	760.0	1080.0	2.0	70.0	40.0
YW 82b	290.0	31.0	126.0	28000.0	780.0	1020.0	2.0	69.0	38.0
YW 83a	197.0	29.0	106.0	25000.0	400.0	900.0	2.0	37.0	33.0
YW 124a	415.0	38.0	410.0	25500.0	2060.0	975.0	5.0	35.0	77.0
YW 125a	680.0	57.0	650.0	40000.0	3740.0	1825.0	7.5	66.0	121.0
YW 126a	645.0	54.0	530.0	40500.0	3160.0	1950.0	6.0	59.0	103.0
YW 127a	830.0	55.0	590.0	60500.0	3660.0	2450.0	7.0	68.0	111.0
YW 128a	605.0	73.0	305.0	43000.0	2900.0	2150.0	4.0	52.0	69.0

\* Denotes Fe rich sample.

# APPENDIX 4

YARNER WOOD DATA FOR ALL SITES									
9 ELEMENTS									
ALL VALUES IN PPM.									
LOCALITY	Cu	Pb	Zn	Fe	Mn	As	Cd	Co	Ni
1	330.0	32.0	90.0	52000.0	490.0	2200.0	2.0	38.0	23.0
2	340.0	34.0	120.0	82000.0	630.0	2820.0	1.5	60.0	33.0
3	290.0	37.0	100.0	53000.0	340.0	3080.0	1.5	33.0	27.0
4	435.0	37.0	108.0	67000.0	840.0	2680.0	1.5	67.0	27.0
5	520.0	37.0	100.0	69000.0	680.0	2900.0	2.0	53.0	30.0
6	490.0	39.0	124.0	97000.0	550.0	4220.0	2.0	55.0	35.0
7	410.0	38.0	80.0	53000.0	500.0	2780.0	1.0	41.0	26.0
8	310.0	37.0	68.0	45000.0	170.0	2340.0	1.5	31.0	24.0
9	131.0	54.0	102.0	24000.0	184.0	680.0	1.0	25.0	23.0
10	870.0	50.0	156.0	66000.0	2030.0	3980.0	3.0	142.0	51.0
11	635.0	48.0	224.0	59000.0	740.0	3940.0	2.0	70.0	41.0
12	535.0	42.0	166.0	52000.0	1200.0	3220.0	3.0	82.0	52.0
13	455.0	41.0	172.0	52000.0	800.0	3040.0	2.5	35.0	43.0
14	435.0	48.0	198.0	55000.0	1330.0	3600.0	2.5	69.0	51.0
15	560.0	39.0	216.0	52000.0	450.0	6300.0	2.5	30.0	37.0
16	400.0	50.0	260.0	59000.0	750.0	8200.0	5.0	84.0	48.0
17	710.0	49.0	260.0	54000.0	2100.0	3560.0	3.5	74.0	64.0
18	595.0	50.0	240.0	61000.0	580.0	7000.0	2.5	46.0	50.0
19	450.0	52.0	232.0	47000.0	1400.0	2460.0	4.0	61.0	78.0
20	335.0	46.0	192.0	57000.0	1120.0	2240.0	3.0	43.0	54.0
21	555.0	64.0	304.0	49000.0	2900.0	2020.0	4.0	67.0	74.0
22	585.0	64.0	310.0	64000.0	3900.0	3000.0	4.5	83.0	96.0
23	660.0	68.0	520.0	68000.0	3700.0	3500.0	6.0	95.0	105.0
24	365.0	54.0	102.0	41000.0	710.0	1840.0	1.5	33.0	36.0
25	1005.0	85.0	1190.0	53000.0	7700.0	2240.0	10.5	146.0	196.0
26	335.0	60.0	212.0	45000.0	970.0	1880.0	2.0	32.0	41.0
27	15.0	10.0	244.0	52000.0	260.0	10900.0	2.5	32.0	23.0
28	535.0	59.0	254.0	31000.0	1750.0	1360.0	4.0	42.0	67.0
29	300.0	51.0	172.0	26000.0	1300.0	1160.0	2.0	27.0	53.0
30	810.0	83.0	266.0	39000.0	360.0	2100.0	3.0	17.0	43.0
31	350.0	74.0	540.0	39000.0	2300.0	1560.0	4.5	43.0	92.0
32	175.0	79.0	580.0	47000.0	5300.0	2440.0	6.0	67.0	149.0
33	154.0	76.0	655.0	42000.0	5600.0	2480.0	6.0	52.0	198.0
34	135.0	70.0	560.0	36000.0	5000.0	2040.0	5.0	69.0	167.0
35	144.0	70.0	565.0	42000.0	5400.0	2220.0	5.5	77.0	160.0
36	145.0	75.0	620.0	50000.0	6400.0	2580.0	6.0	78.0	173.0
37	140.0	77.0	555.0	42000.0	4400.0	2360.0	5.5	71.0	156.0
38	142.0	71.0	540.0	49000.0	5300.0	2920.0	5.5	84.0	161.0
39	170.0	75.0	660.0	64000.0	7900.0	4240.0	6.0	90.0	154.0
40	137.0	71.0	344.0	45000.0	5700.0	2940.0	5.0	76.0	138.0
41	185.0	84.0	520.0	54000.0	6800.0	3420.0	6.0	92.0	171.0
42	190.0	78.0	720.0	49000.0	9600.0	2320.0	6.0	65.0	193.0
43	85.0	33.0	66.0	16400.0	820.0	900.0	2.5	80.0	48.0
44	80.0	32.0	52.0	23000.0	266.0	940.0	1.5	51.0	34.0
45	61.0	25.0	46.0	21000.0	480.0	1280.0	1.5	57.0	39.0
46	120.0	37.0	140.0	15500.0	1100.0	780.0	1.5	192.0	66.0
47	56.0	50.0	52.0	30000.0	220.0	1560.0	1.5	18.0	24.0
48	60.0	26.0	40.0	18400.0	230.0	1080.0	1.5	21.0	29.0
49	70.0	34.0	36.0	26000.0	390.0	920.0	1.5	32.0	29.0
50	50.0	17.0	26.0	2100.0	160.0	120.0	1.5	22.0	22.0
51	125.0	31.0	74.0	7400.0	760.0	160.0	2.5	78.0	48.0
52	139.0	23.0	76.0	7400.0	860.0	120.0	3.5	100.0	42.0
53	149.0	27.0	60.0	9100.0	810.0	220.0	2.5	99.0	46.0
54	135.0	31.0	36.0	8800.0	1100.0	260.0	4.0	109.0	55.0
55	145.0	45.0	44.0	11800.0	1640.0	560.0	2.0	178.0	35.0
56	162.0	40.0	42.0	8900.0	1270.0	160.0	2.5	126.0	35.0

APPENDIX 4 continued over ...

APPENDIX 4 continued

57	152.0	83.0	855.0	57000.0	11200.0	2400.0	6.0	54.0	189.0
58	140.0	95.0	840.0	53000.0	11700.0	2600.0	5.5	49.0	158.0
59	144.0	83.0	1000.0	64000.0	14700.0	4400.0	7.5	71.0	227.0
60	131.0	89.0	850.0	70000.0	15100.0	3480.0	6.0	52.0	136.0
61	120.0	92.0	270.0	24000.0	920.0	400.0	3.0	19.0	60.0
62	130.0	91.0	306.0	15000.0	1010.0	520.0	3.5	23.0	76.0
63	125.0	5.0	950.0	179000.0	18900.0	14300.0	5.0	93.0	200.0
64	90.0	103.0	226.0	15300.0	690.0	200.0	2.0	12.0	33.0
65	160.0	104.0	374.0	29000.0	2400.0	580.0	4.5	27.0	93.0
66	90.0	120.0	306.0	15200.0	1980.0	200.0	2.0	15.0	35.0
67	100.0	130.0	300.0	16200.0	790.0	260.0	2.0	15.0	36.0
68	100.0	140.0	302.0	16200.0	760.0	300.0	2.0	16.0	40.0
69	165.0	30.0	70.0	11800.0	450.0	440.0	2.0	42.0	21.0
70	430.0	35.0	114.0	57000.0	830.0	2520.0	2.5	70.0	32.0
71	22.0	21.0	72.0	12800.0	390.0	60.0	1.0	9.0	13.0
72	22.0	21.0	62.0	11700.0	270.0	80.0	1.5	6.0	11.0
73	35.0	9.0	36.0	7300.0	90.0	60.0	1.0	7.0	19.0
74	225.0	24.0	162.0	22500.0	1010.0	760.0	3.0	81.0	47.0
75	265.0	30.0	182.0	25000.0	760.0	820.0	3.0	71.0	44.0
76	255.0	27.0	146.0	26400.0	680.0	900.0	2.5	66.0	46.0
77	455.0	35.0	128.0	56000.0	1060.0	2080.0	2.5	87.0	37.0
78	510.0	42.0	152.0	53000.0	1400.0	2340.0	3.5	124.0	52.0
79	385.0	35.0	108.0	41000.0	860.0	1600.0	2.5	63.0	36.0
80	54.0	20.0	80.0	9800.0	140.0	200.0	1.0	15.0	21.0
81	35.0	10.0	24.0	5300.0	10.0	80.0	1.0	4.0	10.0
82	235.0	29.0	120.0	28000.0	760.0	1080.0	2.0	70.0	40.0
83	197.0	29.0	106.0	25000.0	400.0	900.0	2.0	37.0	33.0
124	415.0	38.0	410.0	25500.0	2060.0	975.0	5.0	35.0	77.0
125	680.0	57.0	650.0	40000.0	3740.0	1825.0	7.5	66.0	121.0
126	645.0	54.0	530.0	40500.0	3160.0	1950.0	6.0	59.0	103.0
127	830.0	55.0	500.0	69500.0	3660.0	2450.0	7.0	68.0	111.0
128	605.0	73.0	305.0	43000.0	2900.0	2150.0	4.0	52.0	69.0

# APPENDIX 5

```

1      CCLUSTER      CLUSTER - PROGRAM 7.6
2      CROUTINE CLUSTER
5      CCLUSTER ANALYSIS
6      CTHE PROGRAM ACCEPTS AN N BY M DATA MATRIX WHERE N IS THE NUMBER
7      COF OBSERVATIONS AND M IS THE NUMBER OF VARIABLES. IF THE FIRST
8      COPTION OF THE CONTROL CARD IS 1, AN M BY M MATRIX OF SIMILARITIES
10     C BETWEEN COLUMNS IS COMPUTED. IF THE OPTION IS 2, AN N BY N
11     CMATRIX OF SIMILARITIES BETWEEN ROWS IS COMPUTED. IF THE OPTION
12     CIS 3, AN M BY M SIMILARITY MATRIX IS ACCEPTED AS INPUT. IF
13     COPTION TWO IS 1, THE CORRELATION COEFFICIENT WILL BE USED IN THE
14     CSIMILARITY MATRIX. IF THIS OPTION IS 2, THE DISTANCE COEFFICIENT
15     CWILL BE USED. THE PROGRAM LOOPS BACK AND RESTARTS AFTER
16     CCOMPLETION. TO EXIT, READ IN A CONTROL CARD AFTER YOUR DATA
17     C AND SET TO ZERO.
18     C
19     CFORMAT OF CONTROL CARD
20     C      COL. 1-3  0 = END OF JOB
21     C                1 = INPUT A DATA MATRIX
22     C                2 = INPUT A DATA MATRIX AND TRANSPOSE IT
23     C                3 = INPUT A SIMILARITY MATRIX
24     C
25     C      COL. 4-5  1 = CORRELATION MATRIX
26     C                2 = DISTANCE MATRIX
27     C
28     CSUBROUTINES REQUIRED ARE READM, PRINTM, RCOEF, DIST, WPGA,
29     C AND DENDRO.
30     C
31     C=====
32     CPROGRAM CLUSTER(INPUT=101,OUTPUT=201,TAPE5=INPUT,TAPE6=OUTPUT)
33     CDIMENSION X(152,9),IPAIR(2,152),XLEV(152)
34     CDIMENSION A(152,152)
35     CND=152
36     CMM=152
37     CND=152
38     CN=152
39     CM=9
40     C
41     CG... READ CONTROL CARD
42     C
43     C1 READ (5,1000) ITYPE,ISIM
44     C  IF (ITYPE .LE. 0) GO TO 9999
45     C
46     CG... INPUT SIMILARITY MATRIX
47     C
48     C  IF (ITYPE .NE. 3) GO TO 2
49     C  CALL READM(A,M,M,MM,MM)
50     C  GO TO 4
51     C
52     CG... READ AND PRINT INPUT DATA MATRIX
53     C
54     C2 CALL READM(X,N,M,ND,MD)
55     C  WRITE (6,2001)
56     C  CALL PRINTM(X,N,M,ND,MD)
57     C
58     CG... DATA MATRIX LOG-TRANSFORMED
59     C
60     C  CALL LOGTRN(X,N,M,ND,MD)
61     C  WRITE (6,2004)
62     C  CALL PRINTM(X,N,M,ND,MD)
63     C
64     CG... LOG TRANSFORMED DATA MATRIX STANDARDIZED
65     C
66     C  CALL STAND(X,N,M,ND,MD)
67     C  WRITE (6,2003)
68     C  CALL PRINTM(X,N,M,ND,MD)
69     C
70     CG... TRANSPOSE DATA MATRIX (IF REQUIRED)
71     C
72     C5  IF (ITYPE .NE. 2) GO TO 3
73     C    MT=M
74     C    IF (M .GT. 0) MT=N
75     C    DO 110 I=1, MT
76     C      DO 110 J=1, MT
77     C        XS=X(I,J)
78     C        X(I,J)=X(J,I)
79     C        X(J,I)=XS
80     C
81     C110 CONTINUE
82     C    MT=M
83     C    I=1
84     C    J=MT
85     C
86     CG... CALCULATE SIMILARITY MATRIX
87     C
88     C3  IF (ISIM .EQ. 1) CALL RCOEF(X,N,M,ND,MD,A,MM)
89     C  IF (ISIM .EQ. 2) CALL DIST (X,I,M,ND,MD,A,MM)
90     C
91     CG... PRINT SIMILARITY MATRIX
92     C
93     C4  CALL PRINTM(A,M,M,MM,MM)
94     C  WRITE (6,2002)
95     C
96     CG... CALL WPGA(A,I,MM,IPAIR,XLEV,ISIM)
97     C
98     CG... PRINT DENDROGRAM
99     C  CALCULATE AND PRINT LINKAGE TABLE
100    C
101    C  CALL DENDRO(IPAIR,XLEV,M,MM,ISIM)
102    C  GO TO 1
103    C
104    C1000 FORMAT (2I3)
105    C2001 FORMAT (1H,4X,*INPUT DATA MATRIX *,1X,
106    C 1* COLUMNS = VARIABLES, ROWS = OBSERVATIONS*)
107    C2002 FORMAT (1H,4X,*SIMILARITY MATRIX*)
108    C2003 FORMAT (1H,4X,*STANDARDIZED INPUT DATA MATRIX*,1X,
109    C 1* COLUMNS = VARIABLES, ROWS = OBSERVATIONS*)
110    C2004 FORMAT(1H,4X,*LOG-TRANSFORMED DATA MATRIX*,1X,
111    C 1* COLUMNS = VARIABLES, ROWS = OBSERVATIONS*)
112    C9999 CONTINUE
113    C  STOP
114    C  END
115

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APPENDIX 5 continued over ...



# APPENDIX 5 continued

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1      C      SUBROUTINE READM(A,N,M,N1,M1)
C      SUBROUTINE TO READ A DATA MATRIX
5      PARAMETER LIST :
C      A      MATRIX TO RECEIVE DATA
C      N      RETURN'S NUMBER OF ROWS
C      M      RETURN'S NUMBER OF COLUMNS
10     N1     1ST DIMENSION OF A IN CALLING PROGRAM
C      M1     2ND DIMENSION OF A IN CALLING PROGRAM

C      THE DATA IS READ BY ROWS BY ONE OF THREE METHODS
C      A) FIXED FORMAT
15     1ST CARD      COLUMNS 1-3 : NUMBER OF COLUMNS IN DATA
C      COLUMN 7 : 0
C      SUBSEQUENT CARDS : DATA IN FORMAT 10F8.0
C      B) USER-SUPPLIED FORMAT
20     1ST CARD      COLUMNS 1-3 : NUMBER OF COLUMNS IN DATA
C      COLUMN 7 : 1
C      2ND CARD      : DATA FORMAT
C      SUBSEQUENT CARDS : DATA ACCORDING TO FORMAT ON 2ND
C      CARD :
25     C) FREE FORMAT
C      1ST CARD      COLUMNS 1-3 : NUMBER OF COLUMNS IN DATA
C      COLUMN 7 : 2
C      SUBSEQUENT CARDS : DATA, EACH NUMBER SEPERATED BY
C      : SPACE OR COMMA

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C      DIMENSION A(N1,M1),FMT(16)
C      DATA NIN,NOUT,75,6/
35     I=1
C      READ(5,100)NCOL,INTYPE
C      WRITE(NOUT,2001)NCOL,INTYPE
C      IF(NCOL.LT.1)GOTO 900
C      IF(INTYPE.EQ.0)GOTO 101
C      IF(INTYPE.EQ.1)GOTO 102
40     IF(INTYPE.EQ.2)GOTO 103
C      GOTO 901
101    I=1
C      READ(NIN,101) (A(I,J),J=1,NCOL)
C      IF(EOF(NIN))110,101
45     READ(5,100)FMT
102    I=1
C      READ(NIN,FMT) (A(I,J),J=1,NCOL)
C      IF(EOF(NIN))110,112
103    I=1
50     READ(NIN,*) (A(I,J),J=1,NCOL)
C      IF(EOF(NIN))110,103
110    N=I-1
C      IF(N.LT.2)GOTO 902
C      I=NCOL
55     WRITE(NOUT,2000)N
C      RETURN
900    WRITE(NOUT,2002)
60     STOP
901    WRITE(NOUT,2003)
60     STOP
902    WRITE(NOUT,2004)N
60     STOP
1000   FORMAT(I3,3X,I1)
1001   FORMAT(10F8.0)
65     1002  FORMAT(5A10,/,5A10)
2000   FORMAT(/14,14,19H ROWS OF DATA READ)
2001   FORMAT(14H,20H INPUT PARAMETERS PROVIDE FOR,14
70     +,9H COLUMN(S)/24H DATA PREPARED BY METHOD,I2)
2002   FORMAT(/43H ***ERROR*** NUMBER OF COLUMNS LESS THAN 1)
2003   FORMAT(/46H ***ERROR*** ILLLEGAL DATA INPUT METHOD NUMBER)
2004   FORMAT(/14H ***ERROR*** ONLY,12,15H ROW(S) OF DATA)
C      END

```

```

1      CPRINTM      PRINTM - PROGRAM 4-2
C      SUBROUTINE TO PRINT A MATRIX
C      HAVING N ROWS AND M COLUMNS
5      C      SUBROUTINE PRINTM(A,N,M,N1,M1)
C      DIMENSION A(N1,M1)
C      PRINT MATRIX OUT IN STRIPS OF 10 COLUMNS
10     DO 100 I=1,N
C      IE=I+1
C      IF (IE-M) 2,2,1
1     I=M
C      PRINT HEADING
2     WRITE (6,2000) (I,I=IB,IE)
15     DO 101 J=1,M
C      PRINT ROW OF MATRIX
C      WRITE (6,2001) J,(A(J,K),K=IB,IE)
101    CONTINUE
100    CONTINUE
20     RETURN
2000   FORMAT (14H,1X,10I12)
2001   FORMAT (14H,15,10F12.4)
C      END

```

```

1      C      CLOGTRN
C      SUBROUTINE TO LOG TRANSFORM (LOG10)
C      A MATRIX HAVING N ROWS AND M COLUMNS
5      C      SUBROUTINE LOGTRN(A,N,M,N1,M1)
C      DIMENSION A(N1,M1)
C      DO 100 I=1,N
C      DO 101 J=1,M
10     C=A(I,J)
C      IF(C)200,200,201
200    A(I,J)=C
C      GO TO 101
201    A(I,J)=ALOG10(A(I,J))
15     CONTINUE
100    CONTINUE
C      RETURN
C      END

```

# APPENDIX 5 continued

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1      C STAND          STAND - PROGRAM 7.4
C      SUBROUTINE TO STANDARDIZE THE COLUMNS OF A DATA MATRIX
5      C
C      SUBROUTINE STAND(X,N,M,N1,M1)
C      DIMENSION X(N1,M1)
C... STANDARDIZE EACH COLUMN OF THE MATRIX
10     C
C... DO 100 I=1,M
C... CALCULATE MEAN AND STANDARD DEVIATION OF COLUMN
C
C      SX=0.0
C      SXX=0.0
15     DO 101 J=1,N
C      SX=SX+X(J,I)
C      SXX=SXX+X(J,I)**2
101    CONTINUE
20     XM=SX/FLOAT(N)
C      SD=SQRT((SXX-SX*SX/FLOAT(N))/FLOAT(N-1))
C... SUBTRACT MEAN FROM EACH ELEMENT IN COLUMN, THEN
C... DIVIDE RESULT BY THE STANDARD DEVIATION.
25     C
C      DO 102 J=1,N
C      X(J,I)=(X(J,I)-XM)/SD
102    CONTINUE
100    CONTINUE
30     RETURN
END

1      C RCOEF          RCOEF - PROGRAM 7.3
C      SUBROUTINE TO CALCULATE THE MATRIX OF CORRELATIONS
5      C
C      SUBROUTINE RCOEF(X,N,M,N1,M1,A,M2)
C      DIMENSION X(N1,M1),A(M2,M2)
C      AN=N
10     C... CALCULATE CORRELATION COEFFICIENT BETWEEN COLUMNS I AND J
C
C      DO 100 I=1,M
C      DO 100 J=I,M
15     C
C... ZERO SUMS
C
C      SX1=0.0
C      SX2=0.0
20     SX1X1=0.0
C      SX2X2=0.0
C      SX1X2=0.0
C... CALCULATE SUMS, SUMS OF SQUARES AND SUM OF CROSS-PRODUCT
25     C... OF COLUMNS I AND J
C
C      DO 101 K=1,N
C      SX1=SX1+X(K,I)
C      SX2=SX2+X(K,J)
30     SX1X1=SX1X1+X(K,I)**2
C      SX2X2=SX2X2+X(K,J)**2
C      SX1X2=SX1X2+X(K,I)*X(K,J)
101    CONTINUE
35     C... CALCULATE CORRELATION COEFFICIENT AND STORE IN MATRIX A
C
C      R=(SX1X2-SX1*SX2/AN)/
1.  SQRT((SX1X1-SX1*SX1/AN)*(SX2X2-SX2*SX2/AN))
40     A(I,J)=R
C      A(J,I)=A(I,J)
100    CONTINUE
C      RETURN
C      END

1      C DIST          DIST - PROGRAM 7.9
C      SUBROUTINE TO CALCULATE THE MATRIX OF DISTANCE COEFFICIENTS
5      C
C      SUBROUTINE DIST(X,N,M,N1,M1,A,M2)
C      DIMENSION X(N1,M1),A(M2,M2)
C      AN=N
10     C... CALCULATE DISTANCE COEFFICIENT BETWEEN COLUMNS I AND J
C
C      DO 100 I=1,M
C      DO 100 J=I,M
15     C
C... ZERO SUM AND CALCULATE DISTANCE
C
C      DISTX=0.0
20     DO 101 K=1,N
C      DISTX=DISTX+(X(K,I)-X(K,J))**2
101    CONTINUE
C... CALCULATE DISTANCE COEFFICIENT AND STORE IN MATRIX A
25     C
C      A(I,J)=SQRT(DISTX/AN)
C      A(J,I)=A(I,J)
100    CONTINUE
C      RETURN
C      END

```

# APPENDIX 5 continued

```

1      C WPGA          WPGA - PROGRAM 7.7
2      C
3      C SUBROUTINE TO PERFORM WEIGHTED PAIR-GROUP AVERAGE CLUSTERING.
5      C
6      C SUBROUTINE WPGA(X,1,11,IPAIR,XLEV,ISIM)
7      C DIMENSION X(M1,M1),IPAIR(2,M1),XLEV(M1)
8      C DIMENSION I1(168),I2(168),XSIM(168)
10     C... INITIALIZE
11     C
12     C WRITE (6,2001)
13     C DO 100 I=1,M
14     C   I1(I)=I
15     C   110 CONTINUE
16     C   XXXX=-3.0E+35
17     C   IF (ISIM .NE. 1) XXXX=+9.0E+35
18     C   M3=M-1
19     C   IC=0
20     C
21     C... FOR A CORRELATION MATRIX FIND LARGEST SIMILARITY IN
22     C... EACH COLUMN.
23     C... FOR A DISTANCE MATRIX FIND SMALLEST SIMILARITY IN EACH COLUMN
24     C
25     C DO 100 I=1,M
26     C   IF (I1(I) .LE. 0) GO TO 100
27     C   IX=0
28     C   XX=XXXX
29     C   DO 101 J=1,M
30     C     IF (I1(J) .EQ. J) GO TO 101
31     C     IF (I1(J) .LE. 0) GO TO 101
32     C     GO TO (11,12),ISIM
33     C     11 IF (X(J,I)-XX) 101,101,13
34     C     12 IF (X(J,I)+XX) 101,101,13
35     C     13 XX=X(J,I)
36     C   IX=J
37     C   101 CONTINUE
38     C   I2(I)=IX
39     C   XSIM(I)=XX
40     C   100 CONTINUE
41     C
42     C... FOR A CORRELATION MATRIX FIND MUTUALLY HIGH PAIRS
43     C... FOR A DISTANCE MATRIX FIND MUTUALLY LOW PAIRS
44     C
45     C DO 102 I=1,M3
46     C   IF (I1(I) .LE. 0) GO TO 102
47     C   J=I2(I)
48     C   IF (I1(J) .LE. 0) GO TO 102
49     C   IF (I1(J) .EQ. I) GO TO 102
50     C   IF (I1(J) .EQ. 1) GO TO 14
51     C   IF (ABS(XSIM(I)-XSIM(J)) .GT. 0.00001) GO TO 102
52     C
53     C... SAVE PARAMETERS FOR A CLUSTER
54     C
55     C   14 IC=IC+1
56     C   IPAIR(1,IC)=I
57     C   IPAIR(2,IC)=J
58     C   XLEV(IC)=XSIM(I)
59     C   WRITE (6,2002) I,J,XSIM(I)
60     C   I1(I)=0
61     C   I1(J)=0
62     C
63     C... AVERAGE THE TWO COLUMNS
64     C
65     C DO 103 K=1,M
66     C   X(K,I)=(X(K,I)+X(K,J))/2.0
67     C   103 CONTINUE
68     C   102 CONTINUE
69     C
70     C... AVERAGE ROWS THAT WERE CLUSTERED ON THIS ITERATION
71     C
72     C DO 105 I=1,M3
73     C   IF (I1(I) .LE. 0) GO TO 105
74     C   IF (I1(I) .EQ. 1) GO TO 105
75     C   J=I1(I)
76     C
77     C... AVERAGE TWO ROWS IN THE NEW CLUSTER
78     C
79     C DO 106 K=1,M
80     C   IF (I1(K) .LE. 0) GO TO 106
81     C   X(I,K)=(X(I,K)+X(J,K))/2.0
82     C
83     C   106 CONTINUE
84     C   I1(I)=I
85     C   105 CONTINUE
86     C   IF (IC .LT. 13) GO TO 1
87     C   WRITE (6,2003)
88     C   RETURN
89     C
90     C 2001 FORMAT (14I)
91     C 2002 FORMAT (5X,2I5,F15.5)
92     C 2003 FORMAT (1H,4X,'COLUMNS 1 AND 2 -*,1X,
93     C 1 *OBSERVATION IS COMBINED INTO CLUSTERS*,/
94     C 2 5X,'COLUMN 3 - SIMILARITY LEVEL OF CLUSTERING*')
95     C END

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APPENDIX 5 continued

[illegible]



**ABSTRACT**

An investigation of some sources of error in applied geochemical data from South Devon, England. By: Nigel William Radford

Various aspects of analysis by AAS have been investigated. Digestion of 0.5g of minus 125 micron material in 4M  $\text{HNO}_3$  at 95°C for 4 hours seems to be the optimum for such elements as Cu, Pb, Zn, Fe and Mn. Tin determination by AAS, using an air-acetylene flame, is possible, but problems with the ammonium iodide digestion used, remain to be solved. However, the selection of minus 190 micron material as optimum for Sn may be of only local significance.

Some interference effect was observed when different weights of the same samples were analysed, and a spectral interference between Cu and Ag has been detected under certain conditions. Some losses of reproducibility result from evaporation from aqueous digestions after storage for only a few hours in unsealed containers. The postulated presence, in stream sediments, of  $\text{HNO}_3$ -soluble ferric arsenate, and the above digestion, permit As determination by conventional AAS.

Standardised, systematic techniques for such processes as drying and sieving of samples are shown to be necessary in order to achieve good reproducibility.

Partition of error variance has demonstrated that, unless analytical detection limits are approached, sampling error dominates sub-sampling and analytical errors. Various aspects of sampling error have been investigated.

The lowering of AAS detection limits, by the use of flame-less atomisation techniques, means that a case may now be made for the use of acidified natural water samples as a regional as well as follow-up, sampling medium. The dependence of metal partition between sediment and water on physico-chemical properties of the stream has been demonstrated. Therefore, a complete understanding of secondary dispersion can only be achieved if water, as well as sediment, is analysed.

Significant seasonal variations in metal content of both sediment and water samples have been detected and related to the groundwater/surface run-off system.

The data from the main field area, at Yarner Wood, has been evaluated in the context of the mineralisation believed to be present.