ANALYTICAL AND BIOGEOCHEMICAL STUDIES OF TUNGSTEN

A thesis
presented in partial fulfilment of
the requirements for the degree of
Master of Science in Chemistry
at
Massey University

BERTRAM FRANCIS QUIN

1972

"Knowing is not enough
We must apply
Willing is not enough
We must do"

Goethe

ABSTRACT

Section I: Studies were carried out to determine the optimum conditions for the determination of tungsten with a large quartz emission spectrograph. By making use of silver chloride as a carrier, large electrodes and the 2947 A analysis line, soils and rocks containing as low as 10 ppm tungsten could be analysed with reasonable reproducibility. Reliable results were not achieved for plant samples however, and the productivity of the method was very low.

In view of these shortcomings, the use of the dithiol colorimetric reagent for the analysis of tungsten was investigated, and a reliable procedure with a detection limit of 0.1 ppm and very high productivity was developed for the analysis of soils, rocks and vegetation.

Section II: Pot trials were carried out to investigate the uptake of tungsten by young plants of Nothofagus menziesii (silver beech). It was found that, although most of the tungsten taken up from the soil remained in the roots, the concentrations of this element in the leaves, stems and roots of the plants were all related to the tungsten concentration in the soil.

Section III: Biogeochemical and geochemical investigations were carried out in an area of tungsten mineralisation at Barrytown, Westland. The results of preliminary investigations showed that the levels of manganese, tin and lead in the soil were associated with the tungsten level, and may therefore be of possible use as pathfinders for tungsten.

An investigation was carried out to determine whether the concentration of tungsten in plants could be used to predict the concentrations of this element in the soil. It was found that while shallow-rooting species such as tree-ferns could be successfully used to detect soil anomalies, the relationship between the levels of

tungsten in soils and tree species was rather less distinct. Detailed study of trunk and soil samples indicated that this was caused largely by variation in soil properties, particularly pH, which was found to affect the solubility of tungsten.

Despite the unsuitability of trees for indicating concentrations of tungsten in the soil, it was found that tree-trunk analysis could be successfully used to locate tungsten-bearing veins, without restriction in the number and types of species used.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

GENERAL

INTRODUCTION

The term biogeochemistry was first used in 1922 by the Russian scientist Vernadsky, who defined it broadly as the study of the relationships between life, in all its forms, and the geological environment. Biogeochemical prospecting is the application of this concept to prospecting for minerals, by the chemical analysis of plant samples collected from suspected areas of mineralisation, and is based on the general presumption that an anomalous concentration of a metal in the substrate, hopefully caused by the presence of a valuable ore body, will result in an anomalous concentration of that element in the vegetation growing thereon.

The first recorded use of biogeochemical prospecting was in 1936, when trial plant surveys carried out by Palmquist and Brundin of the Swedish Prospecting Company indicated the presence of abnormally high contents of tin and tungsten in Cornwall, and lead and zinc in Wales, in the leaves of trees and shrubs growing in soils containing large amounts of these metals. Unfortunately, apart from a patent covering the technique used (Brundin, 1939) very little of their work was published.

In the years following this early work, there has been a great deal of biogeochemical research carried out, particularly in Russia, where understanding of the factors affecting the success of biogeochemical prospecting has progressed to the stage where all prospecting teams now have at least one biogeochemist included.

Unfortunately, the same is not generally true of Western countries, largely due to a lack of close liaison between mining companies and university research groups. Much excellent biogeochemical research has failed to be applied to prospecting because of a lack of appreciation of, or interest in, the practical requirements of a prospecting method on the part of the scientist. On the other hand, many mining companies, for example in Australia, have tried biogeochemical prospecting for themselves, but because of insufficient study of the factors which can affect the success of the method, obtained poor results and rejected this type of mineral exploration. If biogeochemical

prospecting is to develop further, this situation must be rectified.

In New Zealand, most biogeochemical prospecting research has been based on the assumption that the soil indicates what is in the bedrock, and argues that if plant analysis can be used to indicate what is in the soil, then plant sampling is to be preferred to soil sampling, because the samples are lighter and collection is faster, particularly in areas where the presence of thick layers of forest litter, humus - rich soil and tree roots render soil sampling extremely slow (Brooks and Lyon, 1966). However time has proven that these advantages do not sufficiently outweigh the disadvantages such as the necessity for skilled samplers and the fact that, in many cases, before the concentration of a metal in the soil can be even approximately predicted from its concentration in the plant, several factors such as the soil pH and drainage must be taken into account. Although computerised mathematical techniques incorporating these factors, for example multiple regression analysis, can be used to improve the prediction of soil anomalies from plant data (Timperley, Brooks and Petersen, 1971), this puts biogeochemical prospecting out of the reach of small companies, requires still more skilled personnel, and severely reduces its speed advantages.

It seems, therefore, that if biogeochemical prospecting is to be considered by Australasian mining companies as a worthwhile tool in the search for minerals, it must be demonstrated that in certain geological, topographical and climatic environments, it can give more information than soil sampling. For example, the presence of deep soil or an unmineralised overburden, or the effect of leaching or soil creep, can all prevent the presence of mineralisation from being manifested in the upper soil (from where soil samples are taken), or may produce a soil anomaly at some distance from the actual source. The extensive root systems of some tree species can reach and therefore "sample" deep soil and even bedrock thus pinpointing the exact position of ore bodies.

Some work of this nature has been carried out in North America, and recently in Australia (Severne, 1972). For example, Keith (1968) by analysing the covering vegetation in the upper Mississippi valley district, successfully detected lead and zinc mineralisation under an overburden of loess where no soil anomalies were obvious. However, where loess was absent, he found that soil analysis gave better results than plant analysis. Another example is provided by the work of Kleinhampl and Koteff (1966) who found that conifer samples indicated uranium deposits at depths as great as 70 feet. There is, however, very little published work dealing with the success of plant sampling in areas where, because of factors such as high rainfall and rugged topography, leaching, soil creep and landsliding obscure the soil-bedrock relationship.

The application of biogeochemical prospecting has also been hindered by the lack of suitable rapid methods of analysis for some metals. This has been particularly true for tungsten. Although previous workers have studied the tungsten content of plants in relation to biogeochemical prospecting (Palmquist and Brundin, [unpublished] Kovalevsky 1966), the success of their investigations were severely limited by their method of analysis, namely the emission spectiograph. This instrument, besides being relatively slow in operation, is somewhat imprecise and has a poor limit of detection for tungsten, particularly in samples of high alkali-metal content such as plant ash (Mitchell, 1964).

Although the faster and more sensitive colorimetric methods for the determination of tungsten in soils and rocks, using either thiocyanate or toluene - 3,4 - dithiol (dithiol) have been in use for some years (Ward, 1951; North, 1956), they had not been successfully applied to the analysis of vegetation. The thiocyanate method of Aull and Kinard (1940) was too insensitive for the determination of natural tungsten in vegetation, and the dithiol method of Allen and Hamilton (1952) was too slow and insensitive to be suitable for

biogeochemical prospecting. There therefore existed a real need for a rapid, sensitive, and reproducible method for the determination of tungsten in vegetation.

This need became apparent to me some months after the discovery in 1970 of tungsten at Barrytown, Westland, by Carpentaria Exploration, when, with the kind permission and extensive assistance of that company, I began an investigation into the feasibility of biogeochemical prospecting for tungsten in the area.

The area involved in the study is shown in Fig. 0.1, and consists of a granite mass of approximately a square mile in area, which rises from an altitude of approximately 100' at its western extremity to about 1500' in the east, and is surrounded to the north, south and east by hornsfels and greywacke, and to the west by recent surficial deposits. The tungsten mineralisation [a], approximately 98-99% scheelite and 1-2% wolframite, exists in a series of quartz veins containing discreet crystals up to $\frac{1}{4}$" size and as scheelite disseminated in griesen veins and veinlets up to 2-3mm in thickness. The dimensions of the quartz veins are generally obscured, but appear to have a strike length of 100-200' with a maximum vein size of 0.7m, and tend to occur in swarms containing 10-40 veins over a width of 2-3m.

The annual rainfall of the area is high, approximately 110", with maximum and minimum monthly averages of 14" and 4" in October and December respectively, and the leaching resulting from this, in combination with the granite parent rock, has produced a soil poor in nutrients and of low pH. The soil consists of a dark-brown humus-rich A horizon approximately 0.3m in depth, and lighter brown B horizon of extremely variable thickness and lower organic content. Both horizons contain many rock fragments. The vegetation is predominantly Nothofagus truncata (hard beech) and Weimannia racemosa (kamahi), with increasing

[a] Description of mineralisation provided by Mr J.A.C. Painter, Party Leader, Hokitika, Carpentaria Exploration Co. Pty Ltd.

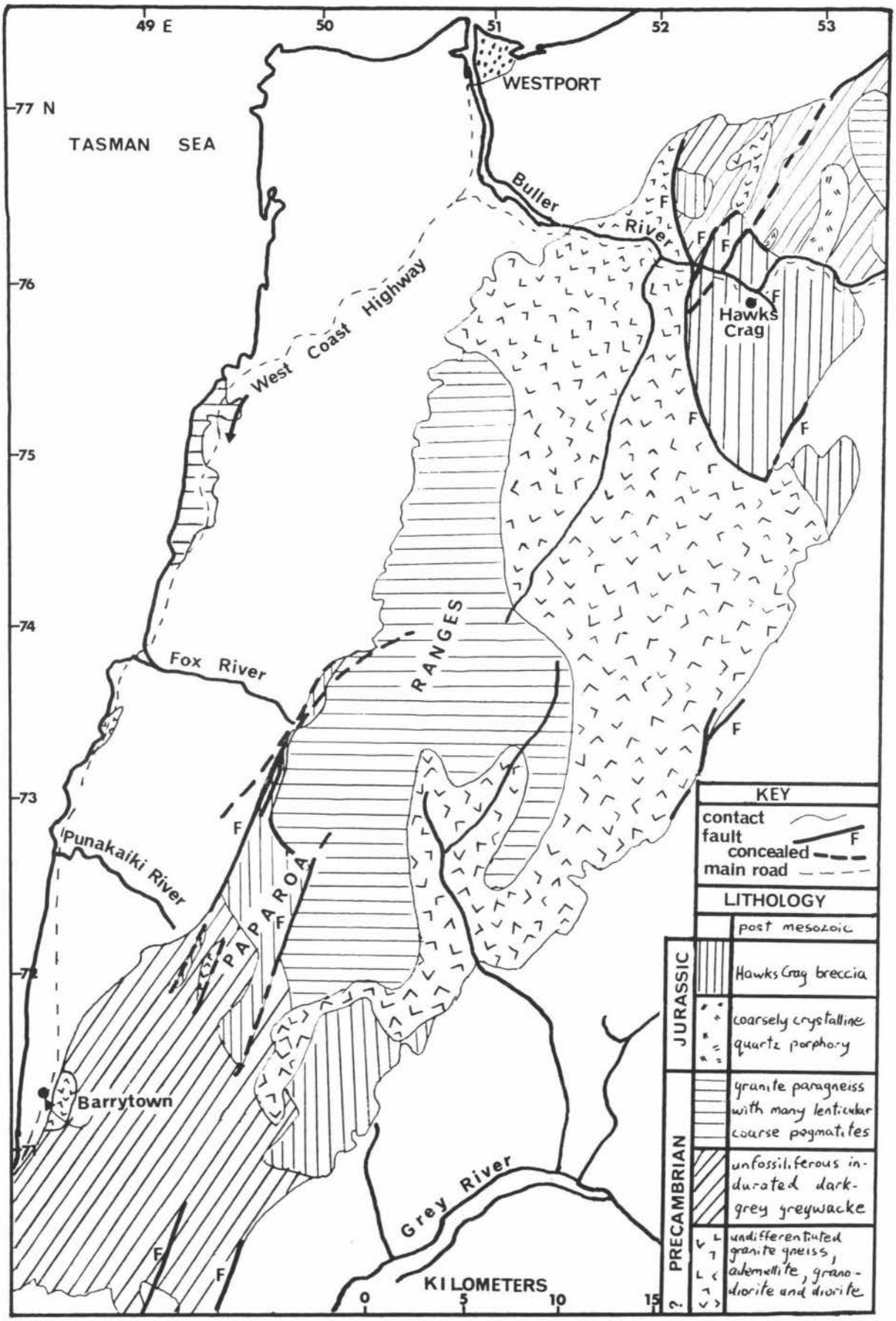


Fig. 0.1. Map showing geology of Paparoa Range.
After Bowen (1964).

dominance of Nothofagus menziesii (silver beech) at higher altitudes. The pale-grey leached A_2 soil horizon, characteristic of the mor- producing beech species, was observed in many flatter areas. Chief secondary species include Quintinia acutifolia and Myrsine salicina, and much of the forest floor is covered in a dense growth of ferns such as the ubiquitous Blechnum discolor (crown fern). The tree ferns Cyathea medullaris (king fern) and Dicksonia squarrosa (wheki) are common on stream banks, as were many smaller ferns such as the Blechnum species.

To conclude this general introduction, the aims of this project may be summarised broadly as follows:

1. To develop rapid, sensitive and reproducible procedures for the determination of tungsten in vegetation, soils and rocks, in any concentration, on a routine basis.

2. To determine whether biogeochemical prospecting has any useful role to play in the detection and pinpointing of tungsten ore bodies, and to compare its success with that of soil sampling, particularly in areas subject to leaching, soil creep and landsliding.

3. To investigate some of the factors which obscure the plant-substrate relationship with respect to tungsten, to assist in the interpretation of future field work.

SECTION I

DEVELOPMENT OF ANALYTICAL METHODS

A. INTRODUCTION

A literature survey carried out at the beginning of this work indicated that, of the methods in use for the determination of tungsten, only colorimetry, and possibly emission spectrography, had any likelihood of fulfilling the requirements of speed, sensitivity and reproducibility.

The emission spectrograph was developed into a quantitative analytical instrument in the late 1920's through the work of Gerlach, Goldschmidt, and others. It had however a very poor sensitivity for tungsten, (for example, Donati (1927) gave a limit of detection of 100 ppm), and hence only ores and concentrates could be analysed with reasonable accuracy. A figure of 69 ppm obtained for the tungsten content of igneous rocks (Hevesy and Hobbie, 1933) was, even in these early days, considered to be too high. In later years, through the use of concentration techniques and carriers the limit of detection was lowered considerably. Because of this and because I had had previous experience with emission spectrography, I decided to investigate the suitability of a quartz optics instrument for the determination of tungsten in soils, rocks and plant materials.

In the early 1930's the colorimetric method for the determination of tungsten with thiocyanate was introduced (Feigl and Krumholz, 1932) and this and modified procedures (Fer' yanchich, 1934; Fer' yanchich, 1937) allowed for the determination of as little as 10 µg tungsten. An improved thiocyanate procedure (Sandell, 1946) provided the first widely accepted figure for the abundance of tungsten in igneous rocks (1.5 ppm). However this improved sensitivity was obtained only through the use of complicated, time-consuming procedures. Also, several workers have criticised the thiocyanate method for its lack of precision and susceptibility to interferences (Norwitz and Codell, 1954; Wood and Clark, 1958; Hobart and Hurley, 1962). The very large number of published procedures (in excess of seventy)

would seem to substantiate these allegations. The thiocyanate method, then, did not appear to be the most suitable colorimetric method for the rapid determination of tungsten at low concentrations.

The early 1940's saw the introduction of a more sensitive colorimetric method employing toluene -3, 4- dithiol, or dithiol (Hamence, 1940; Miller and Lowe, 1940). Later workers applied the method to the quantitative analysis of several specific types of material, and one of the most successful procedures for the analysis of soils was that of North (1956), which allowed for the determination of as little as 1 μg tungsten (4 ppm) at the rate of forty samples per day. More rapid procedures were later developed (Bowden, 1964; Stanton, 1970). It appeared then that the dithiol method was more likely to be suitable for the rapid determination of small amounts of tungsten in plants, soils and rocks, and therefore this method, rather than that using thiocyanate, was chosen for investigation.

Finally a brief investigation was made of the use of atomic absorption spectrophotometry, using a Techtron AA5 model. However while being eminently suitable for the rapid determination of low concentrations of many metals, this method of analysis is unfortunately very insensitive for tungsten (approximately 100 ppm in the original sample using the high - temperature nitrous oxide - acetylene flame). Because of this very poor limit of detection, which is caused by the very refractory nature of its trioxide, atomic absorption spectrophotometry was not considered further.

This section, then, reports on the analytical procedures which were developed for the analysis of tungsten in plants, soils and rocks.

B. EMISSION SPECTROGRAPHY

1. Review of existing procedures

Various methods have been employed to improve the detection limit for tungsten below that of Donati (1927), who detected 100 ppm using an SiO_2 base. Scobie (1943) precipitated tungsten with hydrated Al_2O_3 by means of sodium bicarbonate, and achieved a detection limit of 2 ppm, but Wilson and Fieldes (1944) pointed out that this method was satisfactory only with low Al_2O_3 samples, and preferred a precipitation of tungsten with titanium by means of tannin and antipyrine, which gave a detection limit of 0.7 ppm. However the time-consuming nature of these concentration procedures makes them unsuitable for geochemical exploration programmes requiring rapid analysis.

A detection limit of 10 ppm without prior concentration was reported by Sergeev (1947) who mounted carbon electrodes above the sample, and once the arc was started and the rock powder melted, a magnet placed above the arc caused the vapour to diffuse upward and become excited. However Kaufman and Derderian (1949) achieved a detection limit of 5 ppm in low-grade ores without prior concentration.simply by mixing the specimen with twice its weight of AgCl, which serves to volatilise tungsten rapidly. Because of the simplicity and potential rapidity of this procedure, it was decided to attempt to apply it to the analysis of soils, rocks and plants.

2. Apparatus

The experiments were carried out with a Hilger E742 Large Spectrograph with d.c. arc anode excitation and quartz optics (reciprocal dispersion 12 Å/mm at 4000 Å).

Arcing was carried out in an atmosphere of 80% oxygen and 20% argon to reduce cyanogen emission and background (Cohen, 1969).

An image of the arc was focussed on the slit via a quartz convex lens and the spectra were recorded on Ilford Zenith spectrographic plates developed for 4½ minutes in

in Kodak D 196 developer at 20°C.

A Hilger densitometer with galvoscale calibrated in B- values (Boswell and Brooks, 1965) was used for densitometry.

3. Preparation of standards

Suitable soil/rock and plant ash bases (Mitchell, 1964) were prepared by mixing together in an agate mortar "Specpure" mixtures of SiO_2 63%, Al_2O_3 20%, Fe_2O_3 5%, CaO 2%, MgO 2%, Na_2CO_3 3.5%, K_2SO_4 3.5% and TiO_2 1% for the soil/rock base, and KH_2PO_4 20%, K_2SO_4 20%, K_2CO_3 20%, SiO_2 20%, $CaCO_3$ 9.5%, Na_2CO_3 5%, MgO 5%, Al_2O_3 0.3% and Fe_2O_3 0.2% for the plant ash base. The mixtures were sintered overnight in a muffle furnace at 1100°C, then ground to a fine powder in an agate mortar. $CaWO_4$ was then added to portions of the bases to give concentrations of 3.16, 10, 31.6, 100, 316, 1000 and 3160 ppm tungsten.

After addition of the required proportion of carbon powder or carrier to a weighed portion of the sample, the mixture was loaded into graphite electrodes which were dried at 130°C for 2 hours before arcing.

4. Preparation of samples

(a) Rock and ore samples

These were ground to pass 100 mesh and a weighed portion mixed with the required proportion of carbon powder or carrier before loading into electrodes.

(b) Soil and stream sediment samples

These were air-dried, the 100 mesh fraction collected by dry-sieving, and a weighed portion mixed with the required proportion of carbon powder or carrier before loading into electrodes. After loading, any humus-rich soil samples were heated over a bunsen until all organic material was combusted. This was done to prevent the sample spitting during arcing.

(c) Plant samples

These were dried at 100°C for dry-weight recordings

before being ashed at 500°C in a muffle-furnace. A weighed portion of the ash was then mixed with the required proportion of carbon powder or carrier before loading into electrodes.

5. Improvement of detection limit

(a) Investigation of analysis line

The most sensitive tungsten lines are shown in Table I.1 with their intensities and interfering lines (Meggers et al, 1961; Ahrens and Taylor, 1961).

Of the high wavelength lines, those at 4302.11 Å and 4008.75 Å are suitable only for the determination of tungsten in low-iron samples, because of the presence of interfering iron lines. The 4294.61 Å line is satisfactory for high-iron samples provided a high-dispersion grating spectrograph is used (for example, Kaufman and Derderian, 1949). However because the dispersion of the quartz spectrograph decreases with increasing wavelength, even the 0.48 Å distance between the tungsten and iron lines, is sufficient to cause serious interference, and prevented the use of this analysis line.

Of the low wavelength lines, that at 2944.40 Å is unsuited for high-iron samples because of the presence of an iron line at exactly the same wavelength. The 2551.35 Å line, besides being less sensitive, also suffers slightly from iron interference. The line at 2896.45 Å is rather less sensitive again and is unsuitable because of the presence of a close molybdenum line, an element that is often explored for jointly with tungsten. This leaves only the 2946.98 Å line, which is fortunately fairly sensitive and virtually free from interference, the chromium line at 2946.84 Å being extremely faint.

It is therefore concluded that the most satisfactory line for the determination of tungsten in high-iron samples with a quartz medium-dispersion spectrograph is that at 2946.98 Å. This line is not one of the commonest mentioned in the literature, but has been used by Wilson and Fieldes (1944) and Ivanova (1968).

Table I.1

Tungsten Analysis Lines

W. lines		Interfering lines		
A	Intensity	Element	A	Intensity
2551.35	280	Fe I	2551.09	6
2896.45	190	Cr II	2896.46	6
		Mo I	2896.44	3.5
2944.40	300	Fe II	2944.40	3.5
2946.98	300	Cr II	2946.84	7
4008.75	950	Fe I	4008.87	5
		Ti I	4008.93	80
4294.61	450	Fe I	4294.13	14
		Ti II	4294.12	12
4302.11	240	Fe I	4302.19	200
		Ca I	4302.53	110

(b) Investigation of electrode size

Preliminary experiments were carried out using a 3 to 1 carbon powder to soil/rock base mixture in standard size electrodes (cavity 6mm deep and 1.5 mm diameter). These electrodes gave a detection limit of approximately 100 ppm. Increasing the ratio of sample to carbon powder from 1 to 3, to 1 to 2, resulted inly a slight improvement in the detection limit.

Various sizes of electrodes were then experimented with, and it was found that the largest size that did not suffer from sample spitting and uneven burns during arcing had a cavity 8 mm deep and 3 mm diameter, and gave a detection limit of approximately 50 ppm. Despite this improvement, the detection limit was still too low, and an attempt was made to improve it further by the use of carriers.

(c) Investigation of silver chloride as a carrier

The addition of carriers can improve the detection limit of some metals by converting them to volatile compounds. The metal is then vaporised more quickly, and as less time is required for arcing, background radiation is reduced, allowing lower concentrations of the metal to be detected.

In most geological samples, tungsten is usually fairly volatile during arcing, because of the formation of WO_3, which sublimes quite easily (Ahrens and Taylor, 1961). However to prevent spitting, it was necessary to mix the samples with 2 or 3 times their weight of carbon powder. Besides reducing the actual amount of sample in the electrode, this reduces the volatility of tungsten, probably by the formation of the refractory tungsten carbide. The effect of silver chloride on the volatility of tungsten was investigated using the 316 ppm soil/rock standard. A number of different combinations of silver chloride, standard and carbon powder were arced. During arcing, the photographic plate was racked every 5 seconds, so that the tungsten content of each 5 second interval could be determined. The results, plotted as percentage tungsten volatilised versus

time, are shown in Fig. I.1. The pure standard (Fig. I.1(a)) showed reasonably fast volatility, about 90% of the tungsten being volatilised in $1\frac{1}{2}$ minutes, compared to the 2 minutes required to arc the sample to completion (although less time was required on the many occasions when part of the sample was expelled from the electrode). When the standard was mixed with carbon powder, volatilisation of tungsten was markedly slower (Fig.I.1(b)), taking place largely in the later stages of the arcing, in contrast to the previous case, indicating the formation of tungsten carbide.

When both silver chloride and carbon powder were added to the standard, there was an initial spurt of volatilisation (Fig. I.1(c) and (d)), followed by a slow rise. This indicates that the silver chloride does convert the tungsten into a more volatile compound, possibly WCl_6, but in the presence of carbon powder some of the tungsten remains as the refractory tungsten carbide. The final samples, containing only silver chloride (Fig. I.1(e) and (f)), showed a rapid volatilisation, 98% of the tungsten being volatilised within 40 seconds for the 2 to 1 ratio of silver chloride to standard and within 70 seconds for the 1 to 1 ratio. Besides exhibiting slightly lower volatilisation, the 1 to 1 ratio was prone to spitting, which the 2 to 1 mixture was not. It was concluded therefore that the optimum arcing mixture for tungsten was 2 parts of AgCl to one part of sample, using a 40 second arcing period.

The arcing mixture having been chosen, a series of rock/soil and plant ash standards were arced. The standard curves are shown in Fig. I.2. The curve for the soil/rock standards gave a detection limit of 10 ppm, probably just adequate for the detection of anomalous tungsten concentrations in rocks, soils and stream sediments.

The plant ash standards were however less intense, giving a detection limit of about 50 ppm. This is caused by the high alkali metal content of plant ash, which by lowering the temperature of the arc slows the volatilisation of tungsten. The plant ash - AgCl mixture was also prone to

spitting. The addition of carbon powder improved this, but resulted in an even poorer detection limit. However because of the relatively low iron content of plant ash (approximately 0.1 - 0.2%), this limit of detection could be improved to 30 - 35 ppm by using the more sensitive 4294.61 Å line. While this equalled the detection limit for tungsten in plant ash for the spectrograph method used by Kovalevsky (1966), the very small proportion of natural samples that had concentrations of tungsten higher than this forced the conclusion that the method was just not sufficiently sensitive.

6. Investigation of palladium as an internal standard

The advantage of using an internal standard is that it provides compensation for a variety of errors (Ahrens and Taylor, 1961). Often the basic cause of the error is difficult to control and may influence the intensity of line emission or disturb the accurate measurement of the radiation that has been emitted. In the first category are all those factors influencing arc temperature, such as change in composition of the arc gas and change in length of the arc column caused by wandering of the cathode spot. In the second category are wandering of the arc across the spectrograph slit, failure to time the exposure exactly, and lack of uniformity in photographic development technique. Another advantage of internal standardisation is that it makes it unnecessary to weigh the specimen accurately, as only the ratio of the intensities of the internal standard and analysis element are important.

Kaufman and Derderian (1949) avoided using an internal standard by running a set of standards on every plate (8 samples and 4 standards per plate, each in triplicate). However as this is very time-consuming, the suitability of palladium as in internal standard was investigated.

Sufficient palladium was added to the silver chloride so that its concentration in the analysis mixture was about 100 ppm. The palladium line at 3027.91 Å was chosen for its suitable intensity and lack of interference. Its potential as an internal standard for the determination of tungsten

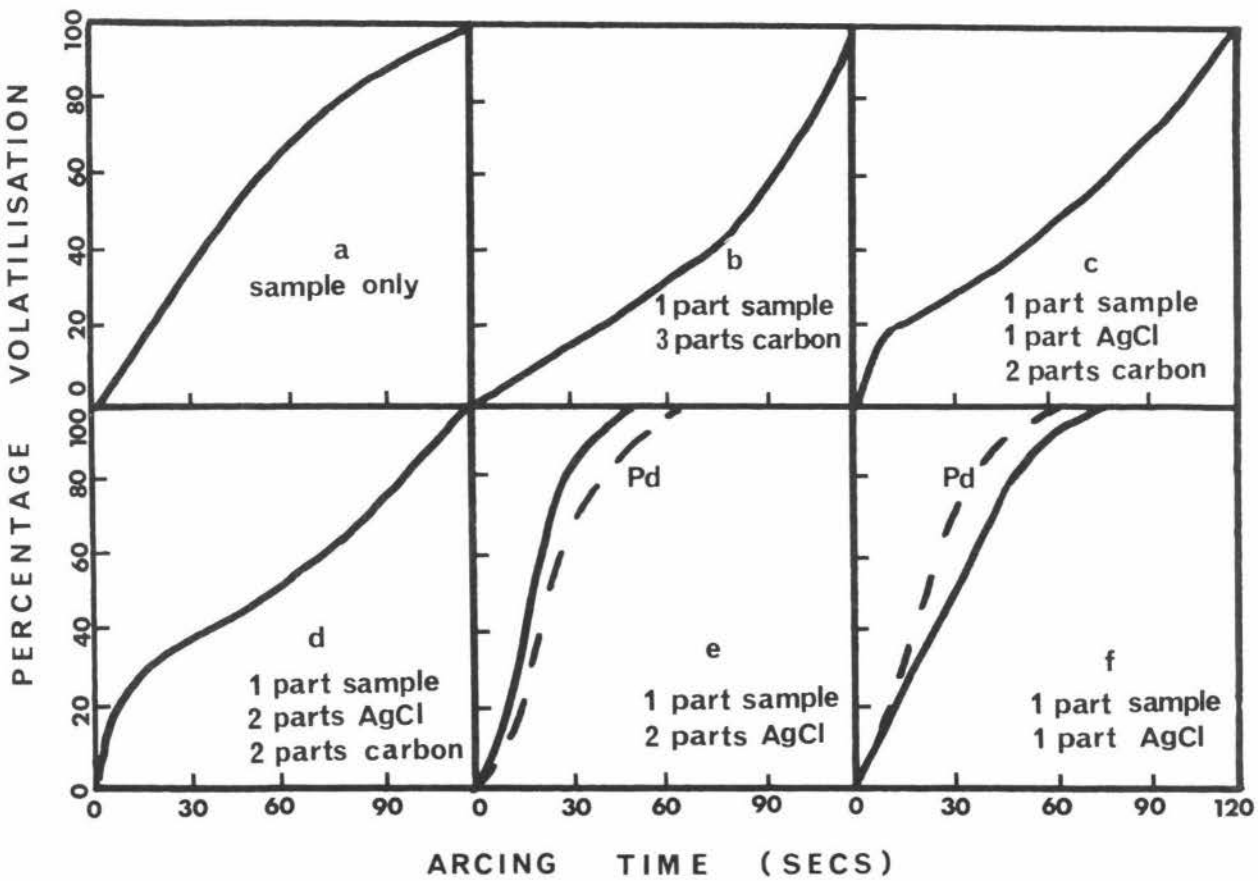


Fig. I.I. Volatilisation curves for tungsten.

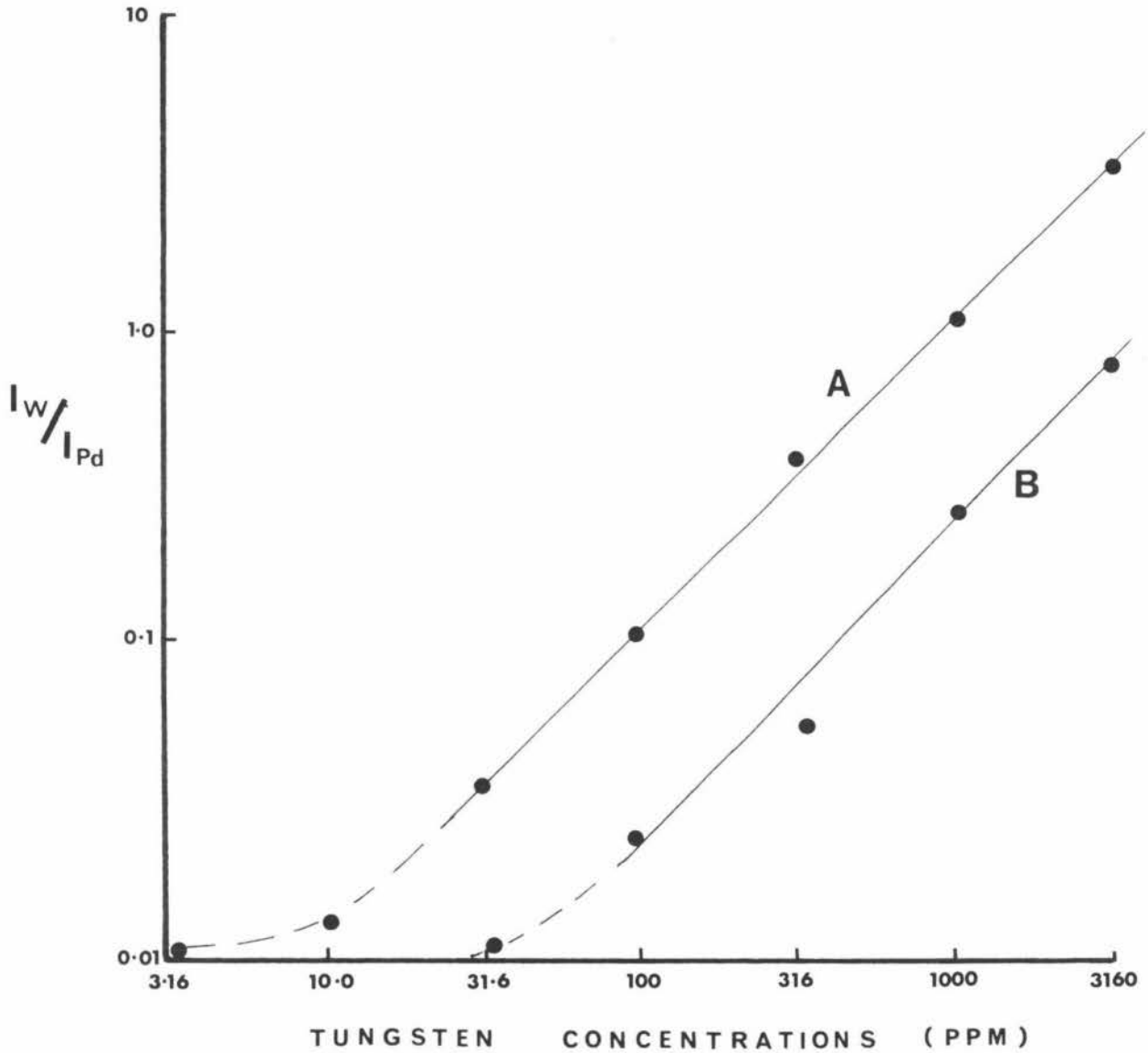


Fig. I.2. Emission spectrograph working curves for (A) soil/rock and (B) plant ash.

was then examined with reference to the several factors summarised by Ahrens and Taylor (1961) which must be considered when choosing an internal standard:-

Factor	Comments
(i) If the internal standard is to be added, its concentration in the analysis elements should be negligibly low;	(i) Palladium was not detected in any of the samples from the study area (limit of detection 10 ppm);
(ii) The rates at which internal standard and analysis element volatilise should be very similar;	(ii) The rates of palladium volatilisation are included in Fig.I.1. It shows little variation and is very similar to that for tungsten in the AgCl mixture chosen (Fig.I.1(e));
(iii) Internal standard and analysis lines should have similar excitation potentials;	(iii) Excitation potentials are similar, being approximately 4 ev for palladium and 3.5 ev for tungsten;
(iv) The internal standard line should be free from self-absorption;	(iv) The palladium 3027.91 Å line is free from self-absorption at a concentration of 100ppm;
(v) Analysis and internal standard lines should be roughly the same wavelength, so as to reduce errors that might occur in photographic measurement;	(v) The wavelengths of the two lines are very close, being 2946.90 Å for tungsten and 3027.91 Å for palladium;
(vi) If the internal standard is added, it should be in a high state of purity with respect to the elements sought;	(vi) Palladium was added as extremely pure "Specpure" ammonium palladate;
(vii) The ionisation potential of the internal standard and analysis elements should be similar;	(vii) The ionisation potentials are very similar, being 8.33 for palladium and 7.94 for tungsten;
(viii) The atomic weight of the internal standard and analysis elements should be similar, if either is a light element;	(viii) Neither are light elements, palladium having an atomic weight of 106.4 and tungsten one of 183.85;
(ix) If samples of widely variant matrices are to be analysed, the internal standard and analysis lines should vary in a similar way with changes in matrix.	(ix) As all samples were from a granite (high SiO_2) area, changes in matrix did not have to be considered.

As a result of this examination, it was concluded that palladium was ideally suited as an internal standard for tungsten. Although palladium has been used extensively as an internal standard for many other elements, to the author's knowledge it has not previously been used for tungsten, probably because, in the absence of silver chloride, it volatilises more slowly than palladium. Other elements that have been used as internal standards for tungsten include silicon (as SiO_2, Ahrens 1943), cobalt (Raikhbaum, 1939), and nickel (Nedler, 1940).

7. Reproducibility and precision tests

Table I.2 shows the results of replicate analyses of natural rock, soil and plant samples, and background samples containing added tungsten.

The precision and reproducibility of the rock and soil analysis is satisfactory, being less than 15% above 50 ppm. However replicate analyses of plant ash samples were unsatisfactory, partly due to commonly-occurring uneven burning and spitting during arcing (in non carbon powder samples). A further problem with plant ash that was very difficult to overcome was the error caused by the large variation in alkali metal content between plant species, and even within a particular species. Although the internal standard compensated for this to some extent, it did lead to greater error. Multiple analysis of each sample allowed more accurate determination but decreased the speed of analysis.

In conclusion then, it is considered that the method developed has a just-adequate sensitivity, and satisfactory reproducibility, for the determination of tungsten in soils and rocks. However the poor detection limit for plant ash, coupled with the lack of reproducibility, makes this method rather less than ideal for the analysis of tungsten in vegetation.

Table I.2

Reproducibility and Recovery Tests

Sample	Number of Determinations	Spread	Mean	Coefficient of Variation (%)
Soil	5	22-37	28	24.8
Soil	5	54-69	60	14.7
Soil	5	290-360	330	10.1
Soil(200 ppm added)	5	180-230	210	13.3
Rock	5	2000-2450	2310	11.7
Plant	5	40-110	72	49.2
Plant(100ppm added)	5	60-120	83	35.6

8. Final spectrographic operating conditions

Table I-3 gives the final conditions chosen.

Approximately 150 samples, mainly soils, and a few rocks and plants, were analysed using the above conditions. About 25 samples could be analysed per man-day. Tin and molybdenum, which are both very sensitive by emission spectrography, were also determined in a large proportion of the soil samples (analysis lines 2839.99 Å and 3170.35 Å respectively).

9. Conclusion

Because of the unsuitability of emission spectrography for the determination of low concentrations of tungsten in plant ash, and because of the time-consuming nature of this method of analysis, an investigation, described in the next section, was carried out to determine the suitability of dithiol for the rapid analysis of small concentrations of tungsten.

Table I.3

Spectrographic Operating Conditions

Excitation	Anode	
Electrodes	Johnson-Matthey graphite (cavity 8mm deep x 3 mm diameter)	
Sample Matrix	2 parts silver chloride to 1 part sample	
Internal standard	Palladium (100 ppm)	
Arc gap	4 mm	
Gas	20% argon/80% oxygen	
Optical system	Image of arc focussed at slit with F958 convex quartz lens	
Current	7 A d.c.	
Exposure	40 seconds	
Slit width	0.015 mm	
Slit length	12 mm	
Wavelength range	2800-5000 Å	
Photographic plates	Ilford Zenith	
Photographic processing	$4\frac{1}{2}$ minutes at 20°C in Kodak 19b Developer	
Analysis lines	Palladium	3027.91 Å
	Tungsten	2946.98 Å
	Molybdenum	3170.35 Å
	Tin	2839.99 Å

C. COLORIMETRY

1. Review of existing procedures

The term "dithiol" was first applied to toluene -3, 4 -dithiol by Clark (1937), who used it as a reagent for tin, with which it forms a red complex. In 1940 Hamence reported the use of the compound as a reagent for the detection of tungsten and molybdenum, with which it forms blue-green and yellow-green complexes respectively. At the same time its reactions were under investigation by Miller and Lowe (1940) for the analysis of the tantalum and tungsten groups of the Noyes and Bray qualitative scheme. Miller (1941) found that rhenium also forms a green complex with dithiol. Later (Miller, 1943), she stressed the importance of the reagent for detecting tungsten in the presence of large amounts of aluminium, beryllium, chromium, uranium, vanadium, zinc and phosphate, and reported the possible use of the reagent for quantitative measurement of tungsten, by dissolving the first-formed precipitate of tungsten, - dithiol in n-butyl acetate which gave a detection limit a $1\mu g$.

For the detection of tungsten in the presence of molybdenum, Hamence (1940) recommended the prior removal of molybdenum by precipitation with hydrogen sulphide. However Miller (1944) reported that a preliminary reduction with tin (II) chloride suppresses the reactions of molybdenum and rhenium with dithiol without affecting its reaction with tungsten, and recommended the development of the test for the quantitative analysis of tungsten.

Specific procedures for the quantitative determination of tungsten in various types of material were soon forthcoming. Following the report of Wells and Pemberton (1947) that cold, dilute hydrochloric acid solutions favour the formation of the molybdenum-dithiol complex, and that the complex could be extracted into amyl acetate, Bagshawe and Truman (1947) employed this procedure in their method for the determination of tungsten in steel. Once the molybdenum had been removed from the sample solution, the tungsten

complex was extracted from the hot strongly-acidified solution.

Bickford et al (1948) determined tungsten and molybdenum in pharmaceutical products by firstly adding citrate to suppress the reaction of tungsten with dithiol in sulphuric acid solution, during the production and removal of the molybdenum complex, then decomposing the citrate by digestion with sulphuric acid before estimation of the tungsten.

Allen and Hamilton (1952) determined molybdenum and tungsten in biological materials using a long and involved procedure incorporating the extraction of the cupferrate complexes of the two metals, followed by precipitation and extraction of the molybdenum - and tungsten - dithiol complexes respectively.

One of the first workers to apply the dithiol test to the analysis of tungsten and molybdenum in geochemical samples was P.G. Jeffery. In his method for the analysis of silicate rocks (Jeffery, 1956), fusion with sodium hydroxide under oxidising conditions was used to extract the elements as the soluble tungstate and molybdate respectively. Silica was removed by evaporation of the alkaline solution with hydrochloric acid, and the complexes of the two metals with α-benzoinoxime were then extracted. When the elements were present in similar proportions, their dithiol complexes are formed in the acid solution and extracted together into light petroleum for photometric measurement at 630 nm (tungsten) and 680 nm (molybdenum). If the proportion of either element greatly exceeded that of the other, the procedure of Allen and Hamilton (1948) was applied for the separation of molybdenum from tungsten.

In the same year North (1956) published his very successful field methods for the determination of tungsten and molybdenum in soils. The soils were fused with a modified low-temperature carbonate flux, the melts were leached with water, and aliquots of the aqueous extracts used for the determinations. At high temperatures (about

100°C) the blue-green tungsten-dithiol complex is extracted selectively into isoamyl acetate from concentrated hydrochloric acid solutions containing tin (II) chloride, which prevents the formation of the molybdenum complex. At low temperatures (20-25°C), the yellow-green molybdenum-dithiol complex is extracted selectively into isoamyl acetate from dilute hydrochloric acid solutions. After the isoamyl acetate has volatilised down to a small globule, kerosene was added and the colour of the organic phase compared visually with a series of standards.

This method, which allows for the determination of 4-400 ppm tungsten and 1-100 ppm molybdenum in soils (greater amounts of both may be determined after dilution), has reasonable sensitivity and rapidity (40 samples per day), and as a result, has served as the basis for most subsequent dithiol procedures for the determination of tungsten and molybdenum in geochemical samples, most of which have been specifically for either tungsten or molybdenum. Modified procedures for the determination of tungsten in geochemical samples include that of Bowden (1964) who criticised North's use of a solution of dithiol in isoamyl acetate, preferring the addition of dithiol as an aqueous, alkaline solution (after Jeffery, 1956), and subsequent extraction of the tungsten complex into an organic phase for comparison with standards. Stanton (1970) criticised North's alkaline fusion, preferring the use of potassium hydrogen sulphate, and, also using an aqueous dithiol solution, streamlined the technique to allow the analysis of 100 samples per day.

However, despite the abundance of published procedures for the determination of tungsten in many types of materials, the only published method which was applicable to the analysis of vegetation is that of Allen and Hamilton (1948), whose method, besides being very slow, was designed only for the determination of tungsten in the range 10-30μg, and is therefore totally unsuitable for the needs of biogeochemical prospecting, which would require a rapid method with a detection limit preferably as low as

1 ppm in ashed vegetation.

Besides the need for a suitable method for the determination of tungsten in vegetation, there was definitely room for improvement in the existing procedures for the analysis of geochemical samples. As the abundance of tungsten in many rocks and soils is only 1-2 ppm (Hawkes and Webb, 1961), an analytical method should ideally be able to detect concentrations of tungsten at least down to this level. However of the existing procedures with sufficient rapidity for the needs of modern geochemical prospecting, none are capable of detecting tungsten at these concentrations.

In conclusion, the aim of this section was to develop rapid and reproducible procedures for the determination of as little as 1 ppm tungsten in plants and geochemical samples.

2. Development of the method

In general terms, the three major points requiring investigation were (i) preparation and decomposition of the sample, (ii) formation and extraction of the tungsten - dithiol complex, and (iii) elimination of interferences.

(a) Preliminary treatment

On arrival in the laboratory, plant samples were removed from their plastic bag containers and dried overnight at 100°C in paper bags.

Although soil contamination is a possible source of error in plant analysis (Mitchell, 1960) this was assumed to be of very minor importance in the area surveyed since there was little exposed soil, a dense vegetation canopy and a relatively high rainfall. Generally however, plants samples were given a preliminary washing.

Soil samples were removed from their plastic bag containers and air-dried. A light crushing was generally necessary to separate aggregated particles. The desired size fraction was then removed by dry sieving with a nylon mesh sieve.

Steam sediment samples were also sieved after air-drying, while rock samples were ground to pass a 100 mesh sieve.

(b) Ashing of vegetation

For colorimetric analysis, it is necessary for the sample to be in solution and for plant samples there are two main ways of achieving this:

(i) dry ashing at 430° to 500°C in a muffle furnace, and

(ii) wet ashing with mixtures of concentrated perchloric, nitric and sulphuric acids at approximately 100° (Allen and Hamilton, 1952).

The choice between these two methods depends on the volatility of the element concerned. For example, if volatile metals such as arsenic, selenium or mercury are to be determined, it is necessary to use the wet method since these metals are all vaporised to varying extents at dry ashing temperatures. Other less volatile metals such as lead, zinc and cadmium can also be partly lost during dry ashing (Mitchell, 1964).

Tungsten however is one of the least volatile metals, having a boiling point of approximately 5900°C. Similarly, none of its compounds that could conceivably be formed in plant ash during dry ashing, for example WO_3 and WC_2, are at all volatile at 500°C.

In view of this, the dry ashing method at 500°C was adopted in preference to the wet ashing procedure. Dry ashing also has the advantages that fewer steps are involved, no supervision is required during the period of ashing, and there is no danger of contamination. At 500°C, the ashing period was shorter and the ash was less adhesive than when a temperature of 450°C was used.

(c) Decomposition of geochemical samples

The most commonly used methods of decomposing a sample fall into three categories: alkaline fusion, acid fusion and acid digestion. The choice of sample attack for a specific element is governed by the efficiency with which

it converts that element into a reacting soluble compound and by its amenability to the conditions required by subsequent treatment. All three types have been used in procedures for the determination of tungsten in geochemical samples.

Jeffery (1956) used an alkaline fusion with sodium hydroxide and nitrate in nickel crucibles for the decomposition of silicate rocks. However North (1956) reported poor recoveries of tungsten using this method, possibly owing to its occlusion in the leached residue, which contained a considerable amount of nickel from the crucibles.

Ward (1951) used another alkaline fusion, consisting of equal amounts of sodium carbonate and potassium nitrate in his thiocyanate method for tungsten, but North (1956) pointed out that this was unsatisfactory for the dithiol method because the large amount of nitrite produced by reduction of the nitrate, decomposed the reagent. This author preferred the use of a flux containing five parts by weight of sodium carbonate, four parts of sodium chloride, and one part of potassium nitrate. The sodium chloride present served to lower the fusion temperature of the flux, so facilitating fusion in nickel crucibles over camping stoves used in the field. This fusion mixture was later used by Bowden (1964), who found Pyrex borosilicate test tubes to be satisfactory for the purpose.

An acid fusion with potassium hydrogen sulphate was recommended by Stanton (1970), who showed it to be more effective than the alkaline fusion of North (1956). In view of this, it was decided to investigate the suitability of this method of fusion.

Although acid digestion, for example with mixtures of nitric and hydrofluoric, nitric and perchloric, or perchloric and hydrofluoric should all be as effective as acid fusion, the method has some disadvantages. The use of hydrofluoric acid necessitates the use of polypropylene beakers (they all of course require the use of an effective fume-cupboard), and an acid digestion generally takes an hour or more

compared to a few minutes for a fusion. Finally, the cost of chemicals per analysis is considerably higher for digestion than for fusion.

All the methods of decomposition have the common effect (more complete in some cases than in others) of releasing the very stable tungstate anion from its insoluble forms in the sample (e.g. as $CaWO_4$, $FeWO_4$ or in the silicate-lattice), thus permitting its removal during the acid extraction which follows.

Stanton (1970) used a ratio of four parts of potassium hydrogen sulphate to one part of sample. An investigation was carried out to determine whether this was in fact the optimum ratio for all concentrations of tungsten. The results (Figure I.3) show the ppm tungsten extracted with increase in $KHSO_4$ for three samples of different tungsten concentrations.

For all three samples, the amount necessary to extract the maximum amount of tungsten from a 0.2g sample is 1.0g, or a ratio of five to one.

In samples A and B, the tungsten decreases with further increase in the ratio. This effect, not reported by Stanton (1970), indicates that excess $KHSO_4$ interferes with the reaction of tungstate with dithiol, possibly by the formation of undissociated K_2WO_4 in the concentrated hydrochloric acid leaching solution.

Sample C, because of its very high tungsten concentration, was analysed by taking only a 100μl aliquot of the sample solution. There was therefore too little $KHSO_4$ present to interfere with the formation of the tungsten-dithiol complex, and this is borne out by the absence of a downward trend.

A muffle-furnace fusion temperature of 575^{o}C was found to be very effective for promoting rapid decomposition of the sample, and allowed test-tubes to be re-used 15-20 times before becoming very brittle.

Samples capable of passing through a 100 mesh sieve were generally used, and grinding down to a finer size did

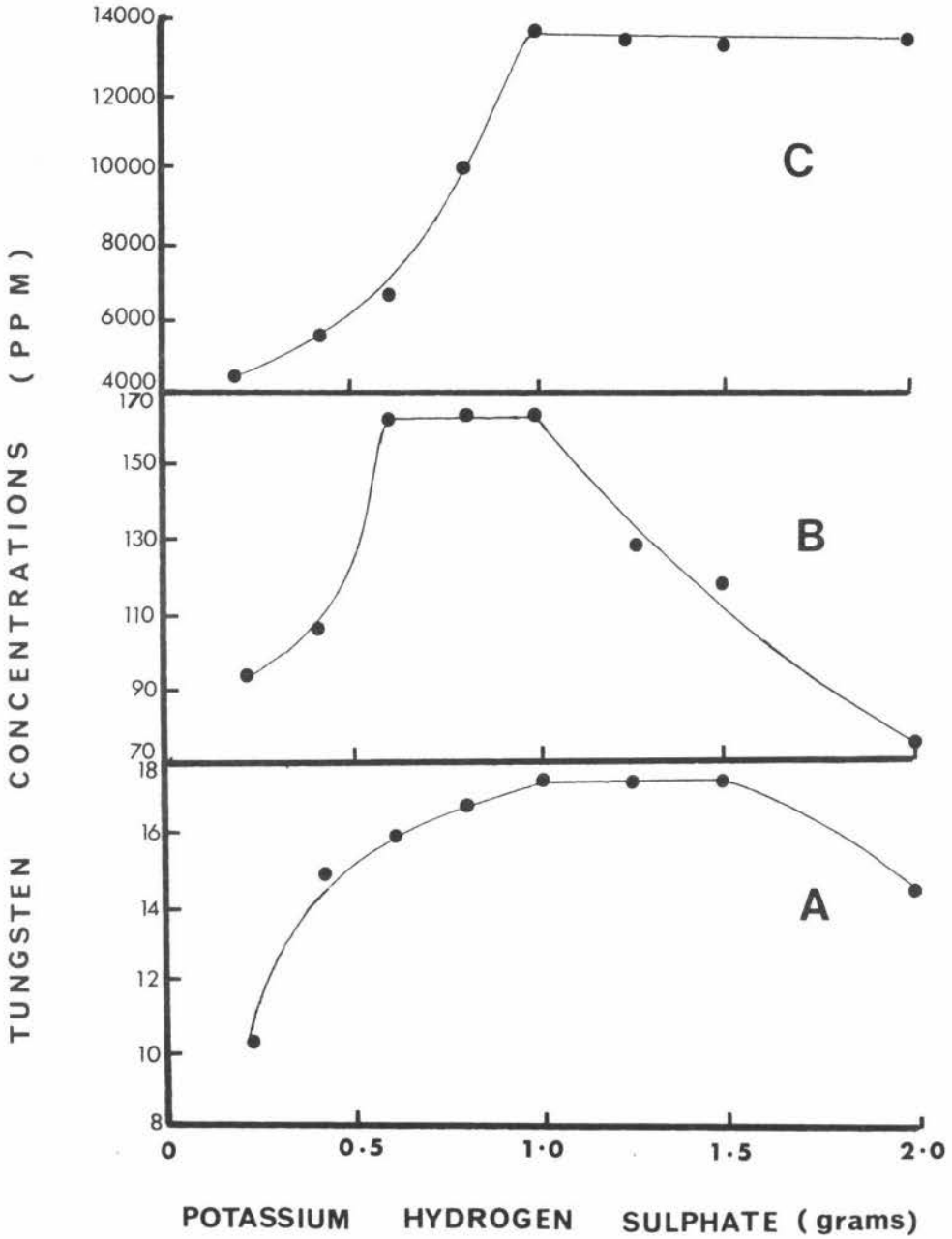


Fig. I.3. Effect of potassium hydrogen sulphate on tungsten analysis.

not increase the result obtained. Particle sizes larger than 100 mesh required a proportionately longer period of fusion.

Table I.4 shows the results of some analyses after decomposition by three methods. The alkaline fusion of North (1956) shows consistently lower values than the acid fusion and digestion methods, which gave excellent agreement. It was therefore concluded that the most effective method of rapidly decomposing geochemical samples was a fusion with five parts of $KHSO_4$ to one part of sample.

(d) Extraction of water-soluble tungsten in soils

A method for the determination of water-soluble tungsten in soils was developed to give some idea of what proportion of the total tungsten in the soil was available to the plant.

Due to variations in the uptake mechanisms of different species, and in the physical and chemical properties of the soil, any method of extraction will give at best only an approximate indication of the proportion of a mineral that is available to the plant at any one time. However, because the clay binding and precipitation of tungstate decreases with pH (Romney and Rhoads, 1966) it was considered that the determination of water-soluble tungsten would give a more accurate indication of natural "available" tungsten than extraction with solutions such as ammonium acetate, acetic acid, disodium ethylerediamine tetraacetate, or dilute hydrochloric acid, all of which control the pH of the sample being extracted.

Water-soluble tungsten was determined by mixing 1 g of soil with 10 cm^3 of deionised water in glass vials for up to 20 hours. Figure I.4 shows the ppm tungsten extracted from four soils. In all cases, 10 hours were sufficient to achieve greater than 90% extraction.

After centrifuging, the solution was filtered through Whatman No. 42 filter paper. The filtrate was then heated

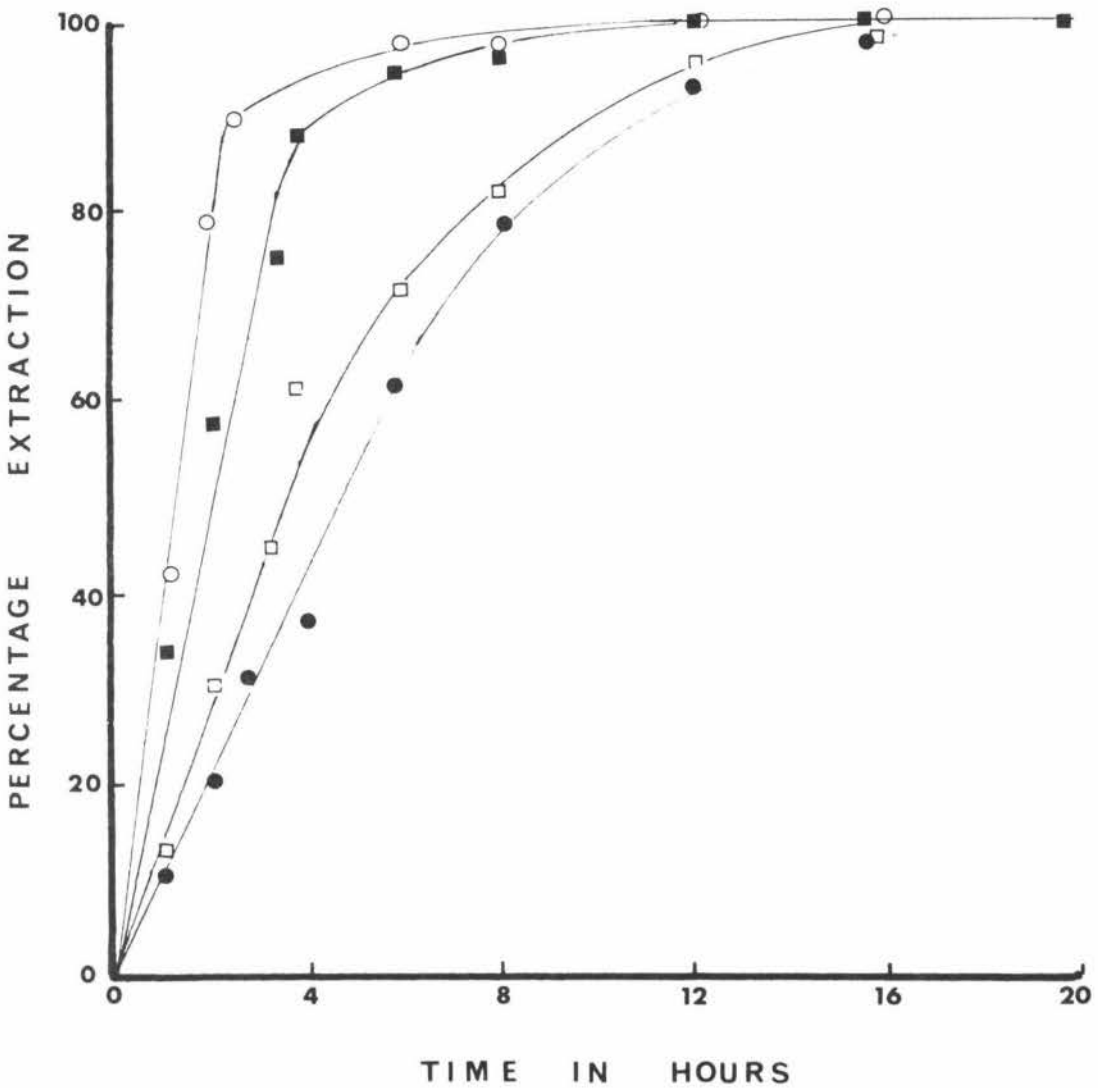


Fig. 1.4. Extraction of water–soluble tungsten vs time.

Table I.4

Comparison of results from different methods of decomposition

Sample	Concentration of tungsten (ppm)		
	Alkaline fusion	Acid fusion	Acid digestion
A	110	140	145
B	115	130	130
C	25	31	30
D	7	15	15
E	95	125	115
F	250	260	270

to dryness to permit the residue to be dissolved in the concentrated hydrochloric acid solution necessary for the subsequent colorimetric determination of tungsten.

Due to the humus-rich nature of the soils, some organic matter was also extracted. As this interfered with the colorimetric measurement by producing a yellow colour in the organic solvent, it was necessary to remove it by means of a quick ashing once the samples had been taken to dryness.

(e) Parameters affecting the formation and extraction of the complex

(i) The nature of the dithiol solvent

In most previous procedures, the dithiol is added to the solution containing the tungsten to be determined in one of two ways. The first involves the addition of dithiol (or its zinc derivative) as an aqueous alkaline solution (Jeffery, 1956; Bowden, 1964; Stanton, 1970). The tungsten-dithiol complex is therefore formed in the aqueous layer and extracted subsequently into an organic solvent such as petroleum spirit for colorimetric determination.

The second type involves the addition of dithiol as a solution in isoamyl acetate (North, 1956). Formation and extraction of the tungsten-dithiol complex takes place simultaneously during a period of heating, which reduces the organic layer to a small globule containing the complex. This globule is dissolved in petroleum spirit for colorimetric determination.

The former method has the advantage of being faster, the formation of the tungsten-dithiol complex being rapid in aqueous solution, whereas in the latter method the reaction can only take place at the aqueous-organic layer interface and is slower as a result. However there seems no doubt that when the dithiol is added as an aqueous solution, either formation or extraction of the complex, or both, are incomplete.

Table I.5 shows the absorbance at 630 nm resulting from the addition of the two types of dithiol solution to a

Table I.5

Comparison of absorbances from 10 μg tungsten using different dithiol solutions

Aqueous dithiol solution	Solution of dithiol in isoamyl acetate
0.261	0.312
0.248	0.318
0.230	0.320
0.228	0.310
0.272	0.310
Average 0.248	Average 0.314

solution containing 10 µg of tungsten. The lower absorbance and inferior reproducibility achieved using the aqueous dithiol solution can only be due to incomplete formation and/or extraction of the tungsten-dithiol complex.

A factor that could cause incomplete formation of the complex is that the tin (IV) present in the solution (from the oxidation of tin (II)) can form tin (IV)-dithiol, thereby competing with tungsten for the dithiol present. When the dithiol is added as a solution in isoamyl acetate this problem does not arise, as the tin-dithiol complex is insoluble in this solvent.

Incomplete extraction may be caused by the use of petroleum spirit as an extractant, whereas in North's method the petroleum spirit is added only once the complex formation and extraction has been completed using the more effective isoamyl acetate.

(ii) Length and temperature of heating

Tungsten is extracted more rapidly into isoamyl acetate at higher temperatures. During heating the solvent is gradually volatilised down to a small globule. Although more isoamyl acetate may be added after cooling for colorimetric determination, it is preferable to use petroleum spirit for this purpose. Besides being less expensive, it has a weaker odour and, because of its lower volatility, samples may be left for a longer period before absorbance measurement.

If volatilisation of the isoamyl acetate is too rapid during heating, extraction of tungsten may not be completed. North (1956) using 150 x 16 mm test-tubes reported that 0.5 cm^3 of isoamyl acetate was reduced to a globule in 15 minutes at 100°C. Even with constant shaking it is doubtful that complete extraction was achieved in this short time, and this is probably partly responsible for the poor reproducibility of North's procedure.

In this investigation, 1 cm^3 of dithiol was volatilised down to a globule in 45 minutes at 85°C in a 115 x 25 mm test-tube, but extraction of 10 µg tungsten

was only 80% complete after this time, and further heating did not complete the extraction. Complete extraction was obtained with 150 x 16 mm and 150 x 12 mm test-tubes, in which average volatilisation times were 3 and 5 hours respectively for 1 cm^3 of isoamyl acetate. At temperatures above 90°C, frequent rapid volatilisation prevented complete extraction.

This reaction time, although long compared to procedures using an aqueous dithiol solution, does not affect the productivity of the method as the reaction is carried out overnight in a water-bath fitted with a constant-filling device. For this reason the smaller size of test-tube (150 x 12 mm) was chosen to allow greater numbers of samples to be treated at once.

Figure I.5 shows the colour development with time from 10 μg tungsten in 150 x 12 mm test-tubes. Once extraction is complete, further heating for up to a week has no effect on the result, the tungsten-dithiol complex being very stable.

Although faster formation of the complex can be achieved by shaking the sample continuously, the overnight heating makes this unnecessary.

Besides ensuring a complete extraction, a long reaction time allows the use of old dithiol solutions. After a period of weeks, or months if stored cool, the solution develops a pale green colour caused by oxidation products of dithiol. This colour can mask low tungsten values, and has been a prime reason for the preference of some workers for the aqueous dithiol solution, which is said to be more stable (Bowden, 1964). However during the long period of heating used in the procedure developed in this project, the dithiol solution is in contact with the reducing solution. This results in the complete removal of the interfering colour, either by reduction or volatilisation (Figure I.5), and removes the necessity to make up fresh solutions at frequent intervals.

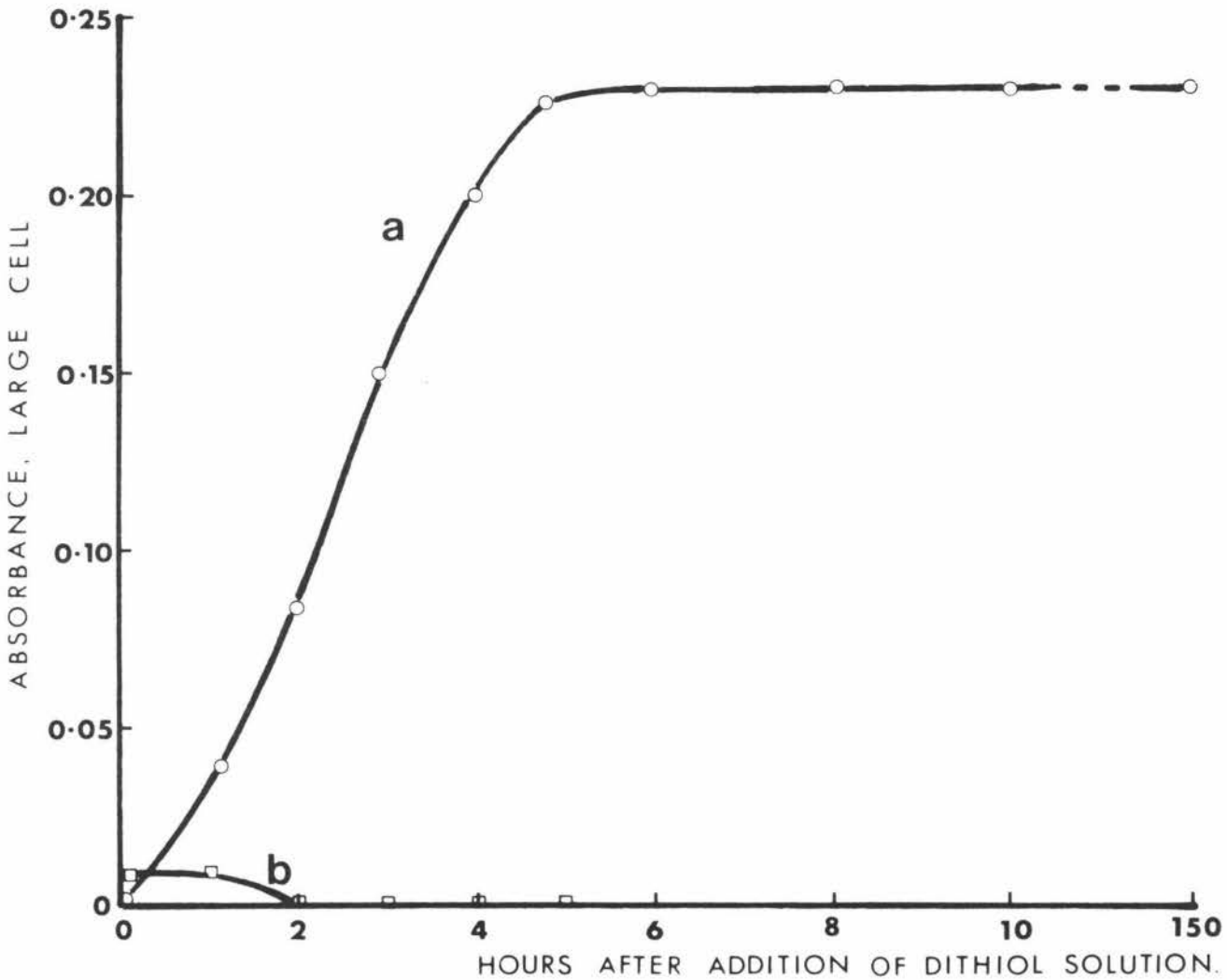


Fig. I.5. Absorbance vs time from (a) 10 μg of tungsten; (b) blank, with old dithiol solution.

(iii) Acidity of the sample solution

As pointed out by Chan and Riley (1966), the formation and extraction of the tungsten-dithiol complex may be carried out in either (a) a hot strongly acidic medium in the presence of powerful reducing agents such as tin (II) chloride, or (b) in a hot weakly acidic medium. No explanation of this behaviour has previously been advanced, however.

Figure I.6 shows the results of an investigation into the effect of acid strength on the formation and extraction of the tungsten-dithiol complex, in the presence and absence of 10% tin (II) chloride (W/V). The low recovery of tungsten in the less acidic solutions of tin (II) chloride is associated with the formation of a pink precipitate of tin dithiol at the aqueous-organic layer interface. As tin (II) is stable in concentrated hydrochloric acid, being air-oxidised to tin (IV) only in less acidic solutions, this suggests that only tin (IV) forms a dithiol complex, and not, as stated by Stary (1964), tin (II).

Further evidence in support of this given by the fact that the addition of a stannic compound to dilute hydrochloric acid results in a red precipitate immediately after dithiol is added.

This does not occur in concentrated hydrochloric acid however, and hence there is no danger of the tin (IV) formed by the reduction of iron (III) consuming the dithiol, provided the acid strength is maintained.

In the absence of tin (II) chloride, complete extraction is attained up to a hycrochloric acid concentration of 4 M (Figure I.6), the percentage recovery decreasing with further increase in molarity. A possible explanation for this is as follows. Normally, the tungsten is present as the stable tungstate anion, the oxygen being lost only when it reacts with the dithiol. However as the acid concentration is increased, so also is the chloride ion concentration, and eventually the tungsten would be more

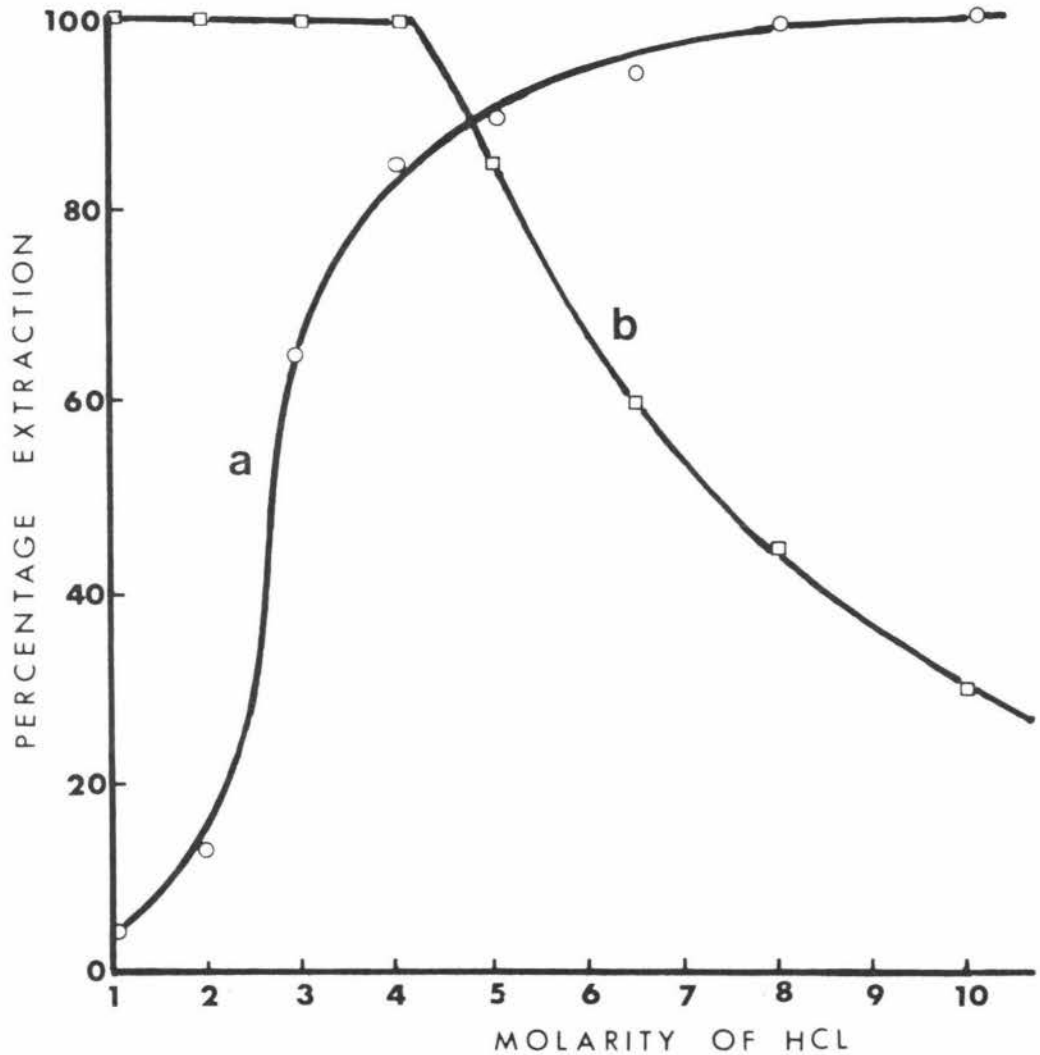


Fig. I.6. Effect of acid concentration on the extraction of tungsten (a) in the presence of 10% tin (II) chloride; (b) in the absence of tin (II) chloride.

stable as a chloro species, such as $WCl_5(H_2O)$ or WCl_6, rather than tungstate or tungsten-dithiol.

In the presence of tin (II) chloride, these chloro complexes would not form, as the tin (II) chloride species would have a much greater attraction for the chloride ions, according to the reaction

$$SnCl_2 + 2Cl^- \rightleftharpoons SnCl_4^{2-} \quad ;$$

and hence complete extraction of tungsten is achieved.

Of the two alternative solutions in which complete extraction of tungsten is obtained, the hot strongly acidic tin (II) chloride solution was chosen because (a) tin (II) chloride suppresses the formation of the interfering molybdenum-dithiol complex (see next section), thereby negating the need for a time-consuming separation, and (b) tests showed that the presence of iron (III) (which tin (II) reduces to Fe (II)), decreases the solubility of the globule in petroleum spirit, and imparts a yellow colour into the organic phase.

By carrying out the leaching of geochemical samples after fusion with 10 M hydrochloric acid, the acid concentration is maintained at this level when the $5cm^3$ aliquot is added to the tin (II) chloride solution, thereby ensuring the stability of the reducing agent and preventing the formation of tin (IV)-dithiol.

(f) Elimination of interferences

Although many metals form dithiol complexes (Clark, 1958), by taking advantage of the wide differences in the solubilities and conditions of formation of the complexes, interference from most metals is completely avoided.

Many of the metals which form dithiol complexes are geochemically rare, for example rhenium (0.005 ppm), mercury (0.08 ppm), platinum (0.01 ppm), palladium (0.01 ppm), and osmium (0.005 ppm). (Figures for crustal abundances from Mason, 1964).

Metals which seriously interfere with earlier procedures include tin, copper, iron and molybdenum.

Interference from tin is prevented by the use of 10 M hycrochloric acid as described in the previous section.

Large amounts of copper can result in the formation of a black copper-dithiol complex. However the use of stannous chloride greatly suppresses its formation, as does the use of a solution of dithiol in isoamyl acetate, as the complex is insoluble in this solvent. The procedure developed therefore has a much greater resistance to copper interference than do procedures using an aqueous dithiol solution (for example, Bowden, 1964; Stanton, 1970).

Large amounts of iron can interfere, both because of the yellow colour of the ferric ion and by the formation of the black iron-dithiol complex. However stannous chloride reduces the ferric ion and suppresses the formation of the dithiol complex, which is also, like the copper complex, insoluble in isoamyl acetate.

In samples of very high iron or copper content (greater than 10 %), some of the black complex may become dispersed colloidally through the organic layer. However even if this should happen, a brief centrifugation is sufficient to completely remove the interference. This problem was encountered in only a few high-iron samples, out of the many hundreds of analyses performed.

Interference from molybdenum poses a more serious threat, as the molybdenum-dithiol complex, besides being a similar colour to that of tungsten (their absorption maxima are at 680 and 630 nm respectively), is one of the few dithiol complexes that are, like the tungsten complex, soluble in isoamyl acetate. The use of tin (II) chloride to reduce interference from molybdenum is incorporated in many procedures for the determination of tungsten with dithiol. Molybdenum, which exists as the molybdate (MoO_4^{2-}) ion in the sample solution reacts with dithiol to form molybdenum (VI)-dithiol (Gilbert, 1956). However, the molybdate ion is more readily reduced than the tungstate ion, and stannous chloride reduces molybdenum (VI) to a

lower oxidation state, probably molybdenum (III), which does not form a dithiol complex. Tungsten remains as tungsten (VI), and its reaction with dithiol is not affected.

Figure I.7 shows the effect of the tin (II) chloride concentration on the extraction of the tungsten and molybdenum complexes. In 10% tin (II) chloride, 100 μg molybdenum (equivalent to 1000 ppm in the original sample) gave an absorbance equivalent to only 0.3 μg tungsten (3 ppm in sample). Lesser amounts of tungsten gave a smaller percentage interference; below 2 μg of molybdenum (20 ppm in geochemical samples of plant ash) there is no interference.

Increasing the tin (II) chloride concentration beyond 10% resulted in a pale yellow colour being imparted into the organic phase. A concentration of 10% was considered therefore to be the most suitable.

The very low percentage interference means that, for prospecting purposes, the method could be assumed to be free from molybdenum interference.

3. Experimental

At the outset of this work, a Hitachi 101 spectrophotometer was used for absorbance measurements. However the simpler and less expensive Bausch and Lomb Spectronic 20 spectrophotometer was found to be just as satisfactory for measurement and faster in operation, and was thus used for all subsequent work. In both cases, large cells requiring approximately 2.5cm^3 of solution for measurement were used, except when more sensitivity was required, in which case 0.2 cm^3 micro cells were used.

A muffle furnace was used for the fusion of soils, stream sediments and rocks, and for the ashing of plants. Fusions could be done over a bunsen flame if only small numbers were being analysed, and plant ashing created less smoke problems if samples were given a preliminary charring on hot plates situated in fume-cupboards.

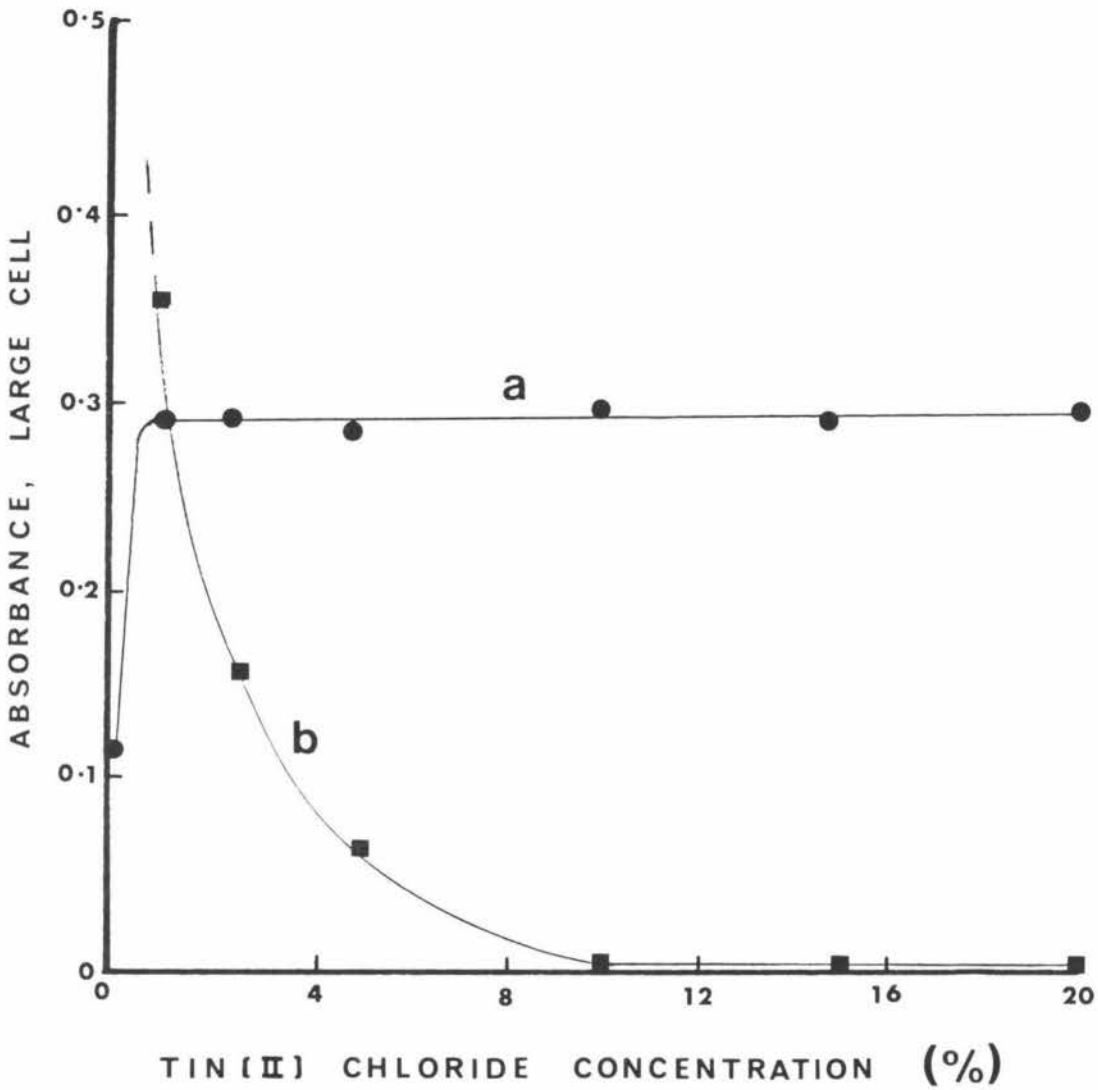


Fig. I.7. Effect of tin (II) chloride concentration on the absorbance from (a) 10 μg tungsten; (b) 100 μg molybdenum.

Sample weighings were carried out on a top-weighing Mettler balance covering the range 0-120 g, with scale divisions every 10 mg.

Pyrex brand borosilicate glassware was used throughout. The heat resistant nature of this glass (melting point approximately 650°C) permitted the use of it for fusions and plant ashing.

4. Reagents

Potassium hydrogen sulphate, fused, A.R.

Hydrochloric acid, 10 M, A.R.

Tin (II) chloride, dihydrate, A.R.

Tin (II) chloride solutions. Prepare 20% (w/v) and 10% (w/v) solutions of tin (II) chloride dehydrate in 10 M hydrochloric acid. Renew solutions every week.

Dithiol (toluene -3, 4- dithiol)

Isoamyl acetate (boiling range 125-142°C)

Dithiol solution. Dissolve the contents of a 5cm^3 ampoule of dithiol in 500 cm^3 of isoamyl acetate. Store in a refrigerator.

Petroleum spirit (boiling range 80-100°C)

Standard tungsten solutions. Dissolve 90 mg of sodium tungstate in 10 M hydrochloric acid and dilute to 500 cm^3 with this acid to give a solution containing 100 μg tungsten per cm^3. From this solution prepare solutions containing 10 μg tungsten per cm^3 and 1 μg tungsten per cm^3 in 10 M hydrochloric acid.

5. Procedures

(a) Determination of tungsten in vegetation

(i) Dry the vegetation to constant weight in beakers at 100°C.

(ii) Char the samples on hot plates if desired, then ash to completion in a muffle furnace at 500°C, cool and weigh.

(iii) Weigh 0.1 g of plant ash into a test-tube (150 x 12 mm, rimmed).

(iv) Add 10 cm^3 of 10% tin (II) chloride solution, and heat in a water bath for 10 minutes at 85°C.

(v) Add 1 cm^3 of dithiol solution and continue heating for a minimum of 6 hours, or overnight, at 85°C.

(vi) Take the test-tube from the water bath, add 1 cm^3(A) or 5 cm^3(B) of petroleum spirit to dissolve the remaining globule of isoamyl acetate.

(vii) Measure the absorbance of the organic phase at 630 nm, by pipetting off as much as required.

(viii) If the absorbance is higher than the highest standard, dilute 1 cm^3 of the organic phase with more petroleum spirit.

Standards. (A) For low range of tungsten concentration. Make a series of standards representing 0, 0.2, 0.5, 1, 2, 5, 10, 20, 40, 60 and 80 ppm tungsten by adding respectively to 11 test-tubes 0, 0.02, 0.05, 0.1, 0.2, 0.5, 1.0, 2.0, 4.0, 6.0 and 8.0 μg tungsten, and continue as in stages (iv) to (vii) of the procedure.

(B) For high range of tungsten concentrations, Make a series of standards representing 0, 2, 5, 10, 20, 50, 100, 200, 400, and 600 ppm tungsten by adding respectively to 10 test-tubes 0, 0.2, 0.5, 1, 2, 5, 10, 20, 40 and 60 μg tungsten, and continue as in stages (iv) to (vii) of the procedure.

Notes. I. Step (i) is not necessary if dry-weight data are not required.

II. An alternative procedure is to weight 2g of dry vegetation into a test-tube, ash the sample and continue as above. The standards will then refer to μg tungsten per 2 g dry weight vegetation, i.e. $\frac{1}{2}$ x ppm dry weight.

(b) Determination of total tungsten in soil, stream sediments and rocks.

(i) Weigh 0.2 g of sample into a test-tube (150 x 12 mm, rimmed).

(ii) Add 1 g of potassium hydrogen sulphate, mix, and fuse in a muffle furnace for 10 minutes at 575°C. Alternatively fuse over a bunsen flame until a quiescent melt is obtained and continue heating for a further 2 minutes.

(iii) Leach in a water-bath with 10 M hydrochloric acid at 85°C until the melt can be broken up with a glass rod.

(iv) Allow to settle, then transfer 5 cm^3 of the clear solution into a test-tube (150 x 12 mm, rimmed) containing 5 cm^3 of 20% tin (II) chloride solution, and heat for 10 minutes at 85°C.

(v) Add 1 cm^3 of dithiol solution and continue heating for a minimum of 6 hours, or overnight, at 85°C.

(vi) Take the test-tube from the water bath, and add 5 cm^3 of petroleum spirit to dissolve the remaining globule of isoamyl acetate.

(vii) Measure the absorbance of the organic phase at 630 nm by pipetting off as much as required.

(viii) If the absorbance is higher than the highest standard, dilute 1 cm^3 of the organic phase by the required amount. However if a dilution of more than 10 times is necessary, analyse instead by taking a small aliquot from the remaining sample solution, making up to 5 cm^3 with 10 M hydrochloric acid, and continue from the addition of the 20% tin (II) chloride solution.

Standards. Make a series of standards representing 0, 2, 5, 10, 20, 50, 100, 200, 300, 400 and 600 ppm tungsten by adding respectively to 11 test-tubes 0, 0.2, 0.5, 1, 2, 5, 10, 20, 30, 40 and 60 μg tungsten. Dilute to 10 cm^3 with 10% tin (II) chloride solution, heat for 10 minutes at 85°C and continue as in stages (v) to (vii) of the procedure.

(c) Determination of water-soluble tungsten in soils

(i) Weigh 1 g of sample into a glass vial, add 10 cm^3 of distilled water, seal and mix for 10 hours.

(ii) Decant the supernatant into a centrifuge tube, centrifuge for 5 minutes, then filter through Whatman No. 42 filter paper (11.5 cm diameter) into a 150 x 12 mm rimmed test-tube, washing the residue with 2 cm^3 of distilled water.

(iii) Take the filtrate to dryness at 110°C, then ash any organic matter at 500°C or over a bunsen flame.

(iv) Add 10 cm^3 of tin (II) chloride solution, and heat in a water-bath for 10 minutes at 85°C.

(v) Add 1 cm^3 of dithiol solution and continue heating for a maximum of 6 hours, or overnight, at 85°C.

(vi) Take the test-tube from the water-bath, and add 5 cm^3 of petroleum spirit to dissolve the remaining globule of isoamyl acetate.

(vii) Measure the absorbance of the organic phase at 630 nm, by pipetting off as much as required.

(viii) If the absorbance is higher than the highest standard; dilute 1 cm^3 of the organic phase by the required amount.

Standards. Make a series of standards representing 0, 0.5, 1, 2, 4, 6, 8 and 10 ppm tungsten by adding respectively to 8 test-tubes 0, 0.5, 1, 2, 4, 6, 8, 10 μg tungsten. Dilute to 10 cm^3 with 10% tin (II) chloride solution, heat for 10 minutes at 85°C and continue as in stages (v) to (vii) of the procedure.

6. Testing of method

(i) Reproducibility tests

Table I.6 shows the results of replicate analyses of some plant, soil and rock samples. The coefficient of variation is less than $\pm$ 11% above 0.1 μg tungsten (1 ppm in geochemical samples and plant ash), which is completely satisfactory for the requirements of mineral exploration, and indeed for most other purposes.

(ii) Recovery tests

Recovery of tungsten added to soil and plant ash samples was complete within the precision of the method (Table I.7).

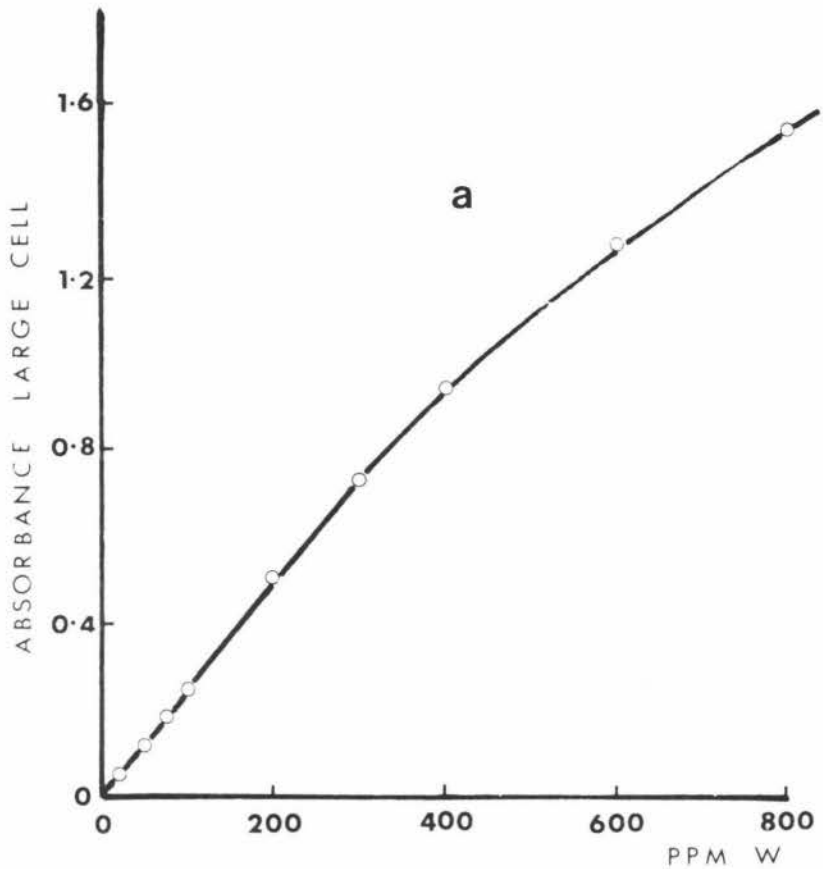
The U.S. Geological Survey standard rock samples G - 1 and W - 1 were analysed by the proposed procedure, with mean tungsten values of 0.5 ppm being obtained for each. These values are in good agreement with the neutron activation results of Hamaguchi et al (1962), who reported 0.50 ppm for G - 1 and 0.58 ppm for W - 1.

(iii) Sensitivity

The proposed procedure allows for the determination of 1 ppm tungsten in soils, stream sediments, rocks and plant ash. Beers law is obeyed up to 300 ppm, and a standard curve is shown in Fig I.8(a).

As background tungsten levels in soils and rocks are about 1 ppm, 5 cm^3 of petroleum spirit is used to allow as wide a range of concentrations as possible to be measured without dilution being necessary. However sensitivity may be improved to 0.1 ppm, or 2 ppm visually in geochemical samples and plant ash by adding only 1 cm^3 of petroleum spirit and using micro-cells for absorbance measurement. This is a significant improvement over the visual detection limit of 4 ppm for Stanton's method, which is only achieved by using 0.5 cm^3 of petroleum spirit. A standard curve is shown in Fig. I.8(b).

Although it was not necessary for this work, the detection limit for tungsten in vegetation could be improved still further by increasing the sample weight used.



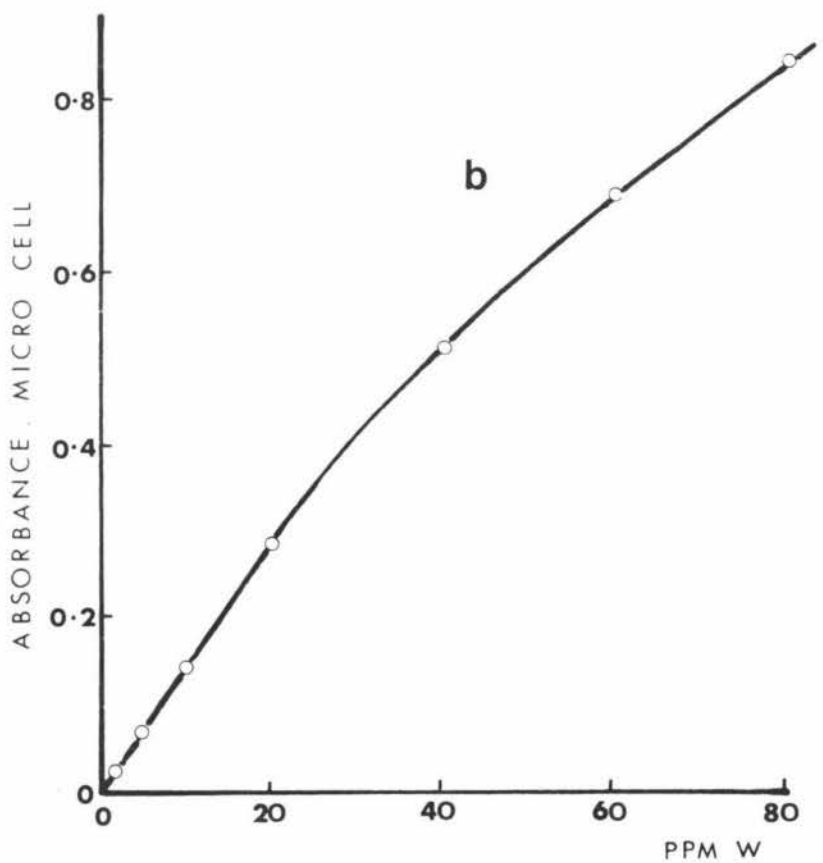


Fig. 1.8. Calibration curves for the colorimetric determination of tungsten (a) in soils, stream sediments and rocks; (b) in vegetation.

Table I.6

Analytical data for replicate determinations of tungsten in plant, soil and rock samples

Sample	Number of determinations	Mean tungsten concentration (ppm)[a]	Range	Coefficient of variation (%)
Plant	4	1460	1300-1600	± 10.4
Plant	4	39.5	37-43	± 6.5
Plant	4	2.9	2.5-3.3	± 4.7
Plant	4	0.27	0.20-0.35	± 24.1
Soil	20	396	350-415	± 4.8
Soil	5	21.4	18-23	± 10.7
Soil	5	1.9	1.7-2.1	± 10.2
Soil	5	1.0	0.9-1.1	± 9.9
Rock	4	13500	13050-13950	± 5.0

[a]plant data are expressed on an ash-weight basis

Table I.7

Recovery of added tungsten from soil and plant ash

Tungsten added (μg)	Tungsten recovered (μg)
1	0.95-1.05
2	1.9 -2.05
4	3.8 -4.1
6	5.8 -6.2
8	7.7 -8.2
10	9.7 -10.3

(iv) Productivity

If a muffle-furnace is used for fusions, upwards of 150 sieved soils, stream sediments or ground rocks may be analysed per man day. Fusing samples one at a time over a bunsen burner would reduce this figure to about 100, which is the productivity of Stanton's method.

Ashed plant samples may be analysed at the rate of 200 or more per man day. The time required to ash the vegetation will vary greatly with different species, plant organs, sample size and sample container.

7. Conclusion

Sensitive and reproducible procedures with extremely high productivity have been developed for the determination of tungsten in vegetation, total tungsten in soils, stream sediments and rocks, and water soluble tungsten in soils.

Although a long reaction time is necessary to achieve the improved sensitivity, this has not affected the productivity of the method as the reaction is carried out overnight.

The development of these procedures made possible the biogeochemical investigations described in the remainder of this thesis. In the course of this project, approximately 2000 tungsten analyses were carried out.

SECTION II

THE UPTAKE OF TUNGSTEN BY NOTHOFAGUS MENZIESII

A. INTRODUCTION

In recent years there has been a growing interest in the effect of tungsten on the metabolism of molybdenum by living organisms. Molybdenum, as molybdate, is known to be an essential element for plants (and animals), and Nicholas and Nason (1955) demonstrated that one of its most important functions was as a constituent of the enzyme nitrate reductase, which reduces nitrate to nitrite. This is an important enzyme because many plants absorb their nitrogen from the soil in the form of nitrate, which must then be converted into the ammonium ion (NH_4^+), before it can be used in the synthesis of amino acids.

Tungsten, as tungstate, has been shown to function as a competitive inhibitor of molybdate uptake and utilisation in Azotobacter vinelandii (Keeler and Varner, 1957), and inhibits growth of those bacteria when nitrate is the sole nitrogen source (Takahashi and Nason, 1957). Tungstate also acts as a competitive inhibitor of molybdate function in the fungus Aspergillus niger when nitrate is the sole nitrogen source (Higgins, Richert and Westerfield, 1956).

More recently, Heimer, Wray and Filner (1969) studied the effect of tungstate on nitrate assimilation in higher plants. They found that tungstate prevented the development of nitrate reductase activity in barley shoots and cell cultures of tobacco, and higher tungstate concentrations had the additional effects of inhibiting nitrate uptake, and preventing root and shoot development in barley. They concluded that tungstate probably acts by inhibiting the incorporation of molybdate into nitrate reductase, rather than by inhibiting the actual formation of the apoenzyme.

Another important role of molybdenum is as a constituent of the enzyme nitrogenase, which is found in Rhizobia, the bacteria that exist in the root nodules of leguminous plants, and are responsible for the conversion of molecular nitrogen to ammonium ions. Plants of this type which have their nitrogen fixed for them are not as dependent

on nitrate reductase.

Tungstate has been found to suppress the function of molybdate in nitrogen fixation in several bacteria strains (Krylova, 1963; Hwang and Doi, 1965), apparently in the same fashion as it does in nitrate reduction. Although this does not seem to have been pointed out in the literature, these findings are in apparent conflict with the results of field tests carried out by Davies and Stockdill (1956). They found that, in the presence of molybdate, the addition of tungstate does not adversely affect the growth of the legume white clover, and, in the absence of molybdate, actually results in an increase in growth, although this increase was less than that produced by an equivalent amount of molybdate. They concluded that tungsten was probably acting as a substitute for molybdenum in its role in nitrogen fixation, although less effectively.

These apparently conflicting results could be explained if it is assumed that during the course of a long field test, the Rhizobia, in the absence of molybdate, could genetically adapt the enzyme nitrogenase to enable utilisation of tungstate instead. To the author's knowledge, no physiological experiments have been performed to determine whether this is so, or to determine whether nitrate reductase could also be adapted to utilise tungstate. Although the problems would be many, this is surely a line of investigation that could yield profitable results for the plant biochemist.

In the meantime, it is of interest to see merely if plants can grow in high soluble-tungstate soils, and to determine how much of this tungsten is absorbed by the plant.

There is in fact very little published work dealing with the effect of the amount of tungsten in the soil on that in plants. This has been caused largely by a lack of suitable methods of analysis for plant materials.

Emission spectrography, because of its poor detection limit (approximately 30 ppm ash weight), has

only allowed for the determination of tungsten in plants growing in highly mineralised areas (Brundin, 1939; Kovalevsky, 1966). Early colorimetric techniques (Aull and Kinard, 1940; Allen and Hamilton, 1952) offered little improvement, and hence have not been employed in biogeochemical studies.

The advent of neutron activation analysis allowed for the determination of incredibly minute quantities of tungsten, and Bowen (1960) found it to be present in various plant tissues in amounts from approximately 0.1 to 3 ppm ash weight. However, the extremely high cost of the instrument, coupled with the time-consuming nature of the technique, makes this method unsuitable for most applications including biogeochemical prospecting.

Romney and Rhoads (1966) studied the uptake of radioactive tungsten - 185 by bush beans grown in soil and nutrient solutions. However because of problems with this technique, such as correcting for decay and self-absorption, their data were presented only as counts / min / g dry plant rather than absolute amounts, or concentrations of tungsten, and hence were of limited value.

The development during this project of a rapid colorimetric method for tungsten (Section I.C), capable of determining as low as 0.1 ppm ash weight, meant that more thorough biogeochemical investigations than had previously been possible could be carried out.

As a preliminary to field work in the area of tungsten mineralisation at Barrytown, pot trials were carried out with young plants of a species common in the area, namely Nothofagus menziesii (Hook. f.) Oerst. (Fag.), to determine (1) whether tungsten can be taken up by plants in significant quantities, (2) in what fashion the absorbed tungsten is distributed between the various plant organs, and (3) whether the tungsten concentration in any of the plant organs is related to the tungsten concentration in the soil.

The results of this investigation are reported in this Section.

B. INVESTIGATION

1. Materials and methods

(a) Setting-up of experiment

The plants used were three-year-old specimens of Nothofagus menziesii (silver beech), which were grown in a standard potting mixture, pH 6.8, in a glasshouse. Their mean height was 30 cm.

Thirteen seedlings were used in the experiment. In order to prevent absorbtion of tungsten on to the walls of the clay pots, the soil (approximately 1 kg in each instance), was encased in a plastic bag with a small drainage hole at the bottom.

Thirteen solutions containing 0-250 mg of tungsten as sodium tungstate were prepared and each was added gradually to the top of the soil over a period of two weeks to produce final concentrations of 2-272 ppm (the potting mixture initially contained 2 ppm tungsten). Individual data for the pots are given in Table II.1.

The pots were placed in petri dishes so that any excess solution was reabsorbed by the contents of the pot. The plants were allowed to take up tungsten for a further eight weeks and then harvested. All plants had remained healthy throughout the experiment.

After harvesting, the soil was shaken from the roots and the plants were thoroughly washed in running water, then divided into roots, stems and leaves. Each plant organ was dried at 110°C to obtain dry weights and then ashed at 500°C. Ashed weights were recorded (Appendix 1).

The tungsten content of the plant ash was determined using the colorimetric procedure described in Section I.C of this thesis. To enable comparison of the distribution of tungsten between the different plant organs with that of known essential elements, copper and zinc in the plant ash were determined by atomic absorption spectrophotometry. This involved simply dissolving the ash in hot 2N hydrochloric acid before analysing.

The soils were partially air-dried, then completely

Table II.1

Data for tungsten in soil

pot no.	dry weight of soil (g).	mg W added	calculated added ppm W[a]	total ppm W
1	970	0	0	2.0
2	760	1.0	0.9	2.9
3	930	1.9	1.9	3.9
4	820	3.9	4.4	6.4
5	970	7.8	7.4	9.4
6	900	15.6	16	18
7	1100	23.5	20	22
8	940	31.2	33	35
9	1120	46.9	42	44
10	790	62.5	80	82
11	940	95.0	100	102
12	990	125.0	125	127
13	940	250.0	270	272

[a]Because average soil dry weight is nearly 1000 g, mg tungsten added corresponds approximately to calculated added ppm tungsten.

dried at 110°C. The concentration of tungsten on a dry-weight basis was calculated from known additions of the element (Table II.1). As a check, tungsten was analysed in one of the soils and a value of 285 ppm obtained for a calculated figure of 272 ppm.

(b) Chemical form of added tungsten

Tungsten exists, virtually without exception, as the tungstate ion in its ores (Rankama and Sahama, 1950). In the area being studied at Barrytown, mineralisation is represented mainly by scheelite ($CaWO_4$), with some wolframite ($(Fe,Mn)WO_4$). These ores are both rather resistant to physical and chemical weathering, but some tungstate is released, mainly by the attack of sulphuric acid in acidic soils, or alkali salts in more basic soils.

Soluble tungsten is therefore represented mainly by the extremely stable tungstate ion, and it is very probable that it is taken up by plants in this form.

For this reason, tungsten was added to the plants as a dilute solution of the very soluble sodium tungstate and not, for example, as finely-ground tungsten metal.

2. Results and discussion

Table II.2 shows the data for the tungsten concentrations in leaves, stems and roots, on dry-weight and ash-weight bases. The low tungsten concentration in the control plant suggests that the background 2 ppm in the potting mixture is in a form relatively unavailable to the plant, possibly $CaWO_4$, as the addition of half this amount (pot 2) as soluble sodium tungstate results in a far greater concentration in the plant.

The data are plotted in Fig.II.1, which shows the relationship between the tungsten concentration in the various plant organs and that in the soil. The results show that, despite the fact that the concentration of tungsten is far higher in the roots than in the aerial parts of the plants, the concentrations of this element in the roots, stems and leaves all follow the level of tungsten in the soil, although the stem, and possibly root,

Table II.2

Data for tungsten concentrations in plant organs

plant no.	ppm W in soil	plants					
		ppm ash weight			ppm dry weight		
		leaves	stems	roots	leaves	stems	roots
1	2.0	4	3	4	0.7	0.2	0.6
2	2.9	12	17	40	0.8	1.0	4.8
3	3.9	9	16	90	0.4	0.8	12.5
4	6.4	9	9	350	0.6	0.5	23.5
5	9.4	28	13	500	1.5	0.6	56
6	18	38	30	900	2.5	1.5	99
7	22	30	65	1150	2.2	3.4	110
8	35	35	38	1300	2.4	2.0	220
9	44	52	80	1650	2.9	5.5	181
10	82	70	95	2300	5.2	5.1	230
11	102	80	80	3500	5.3	5.0	420
12	127	150	90	4300	12.4	5.3	645
13	272	220	160	6000	20.0	9.9	690

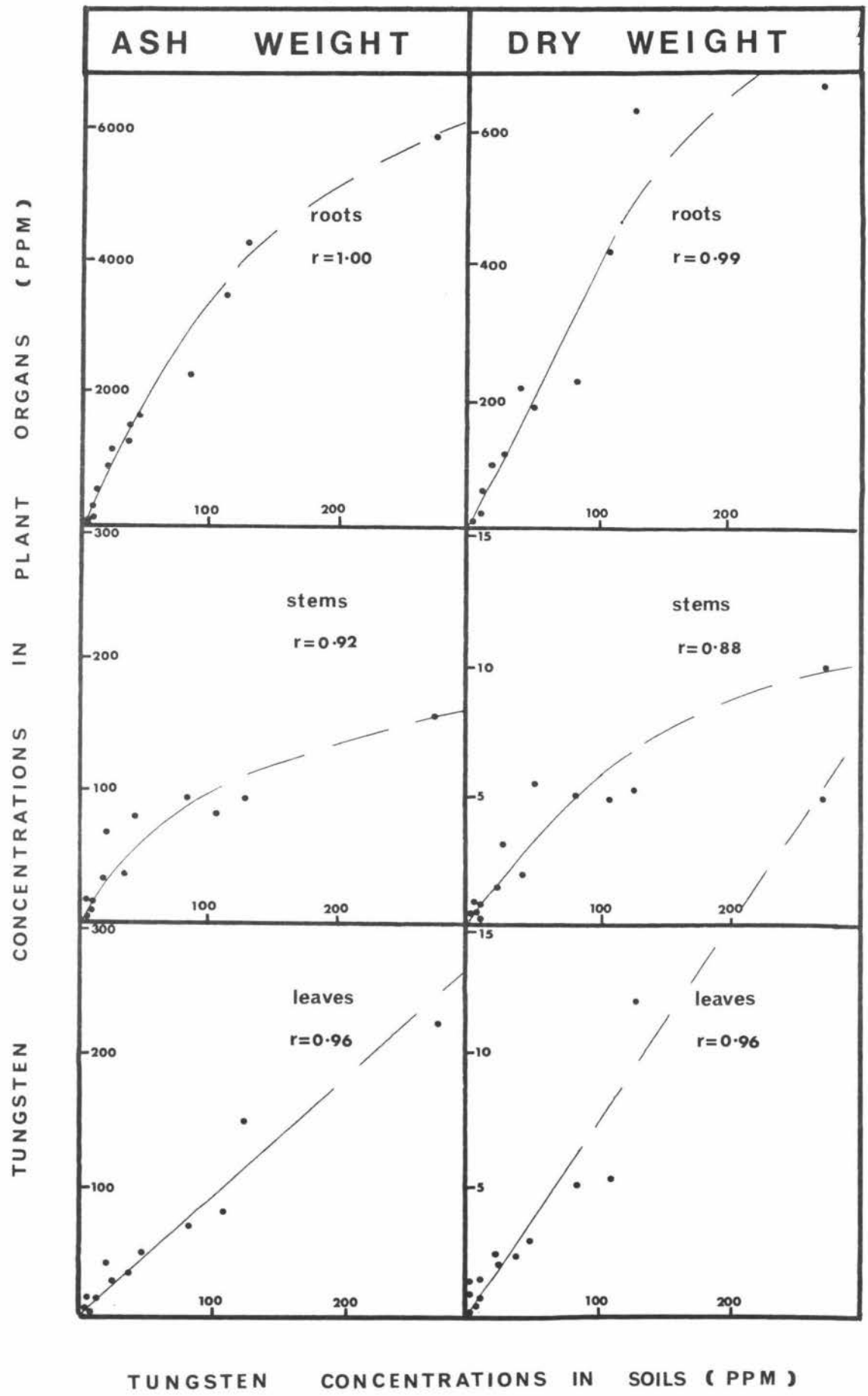


Fig. II.1. Tungsten concentration in the plant organs as a function of the concentration of tungsten in the soil.

concentrations appear to be reaching a limiting value.

The data were tested statistically by the use of the Spearman rank correlation coefficients (r_s). This is suitable for handling small numbers of samples, and does not require the data to be normally or log-normally distributed. The data for one variable are ranked in order of magnitude and the deviation of the data for the other variable from this order are used to calculate r_s, according to the equation (in the absence of tied data):

$$r_s = \frac{6\Sigma d^2}{n^3-n}$$

where n is the number of pairs of data. A value of +1 implies that both components of a number of pairs of data have exactly the same ranking, whereas zero implies a completely random ranking.

The results (Fig. II.1) indicate that ash-weight data gives a better indication of soil concentration than dry-weight data, giving a higher r_s in two of the three cases.

For both ash- and dry-weight data, the value of r_s decreases in the order

roots > leaves > stems

The lower r_s for stems may be due to the fact that much of the tungsten in the stems will be in the process of being transported, and therefore the amount of it actually in the stems at any one time will be more subject to variations in growth rates in individual plants.

The high concentrations of tungsten in the roots relative to the aerial parts of the plants are striking when compared with the concentration of two essential elements, copper and zinc, in the same organs (Table II.3). The average copper concentration in the roots is only 30% higher than that in the leaves and stems, while the zinc concentration is actually 50% lower in the roots. This, plus the fact that the plants growing in the pots containing the most tungsten took up a quantity of this element

Table II.3

Data for copper and zinc concentrations in plant organs

Plant no.	copper			zinc		
	leaves	stems	roots	leaves	stems	roots
1	70	130	160	500	1040	560
2	150	130	115	1340	1300	600
3	110	130	85	900	1100	400
4	170	100	280	2330	1060	800
5	110	115	170	880	1040	400
6	80	110	210	1400	1300	1100
7	210	130	200	1100	1120	600
8	110	85	120	1140	940	420
9	140	180	270	1600	1240	1000
10	150	200	120	1180	1300	540
11	150	120	150	1800	1500	740
12	110	130	140	1300	1340	500
13	160	130	210	1600	1140	640
Average	132	130	171	1313	1186	638

sufficient to give them a higher concentration of tungsten than copper or zinc in their roots, strongly suggests that while the plants do not seem to restrict the uptake of tungsten, there is some mechanism by which transportation of this element from the roots to the aerial parts of the plant can be suppressed. This possibility has also been suggested by Romney and Rhoads (1966), who studied the uptake of radioactive tungsten -185 by bush beans. Although their data were presented only as radioactive counts, they did show that the tungsten concentration in the roots was far higher, perhaps by a factor of 30 - 100, than those in the aerial parts of the plant.

The more similar concentrations of tungsten in the roots and aerial parts of the control plant indicates that, when the tungsten is taken up over a longer period of time, for example since germination, the root concentration effect is possibly not as marked.

Table II.4 gives the data for the total tungsten present in the various plant organs, and gives the percentage of the total added tungsten that has been taken up by the plant.

In contrast with the concentration of tungsten in the plant organs (Fig. II.1), the amount of tungsten taken up does not correlate very well with that added to the soil (Table II.4). To test whether the amount of root material has any effect on the amount of tungsten absorbed, the percentage of the total added tungsten taken up by the plant was plotted against root weight. The results (Fig. II.2) show the presence of a significant relationship, particularly on a ash-weight basis. The relationship is presumeably due to the fact that, the greater the amount of root material, the more soil (and therefore tungsten) it is in contact with.

Table II.5 shows the data for the percentage of the total absorbed tungsten in the various plant organs. Apart from plants 1 and 2, in which the tungsten taken up from that

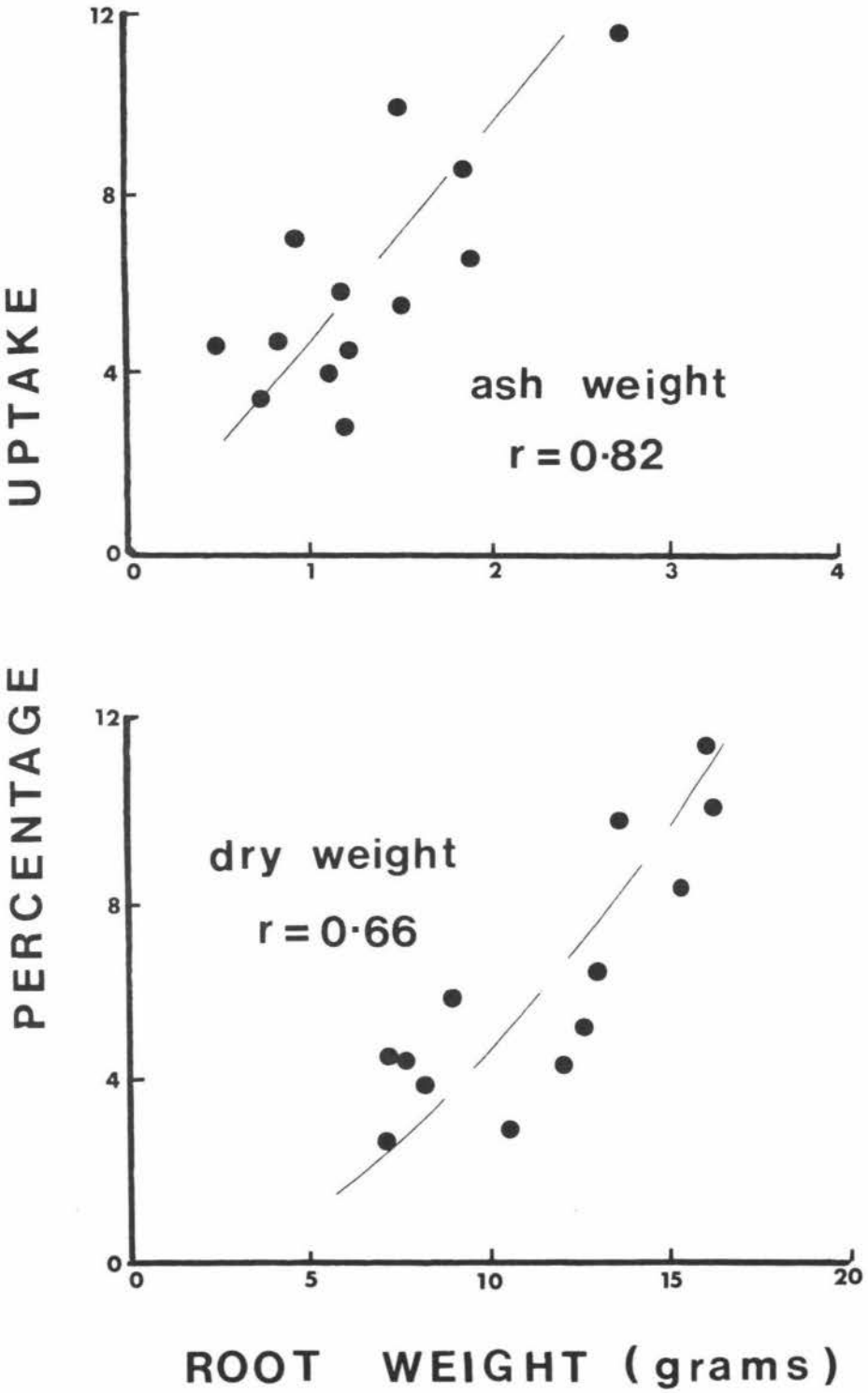


Fig. II.2. Percentage uptake of tungsten as a function of root weight.

Table II.4

Data for tungsten uptake

plant no.	mgW added	µg in leaves	µg in stems	µg in roots	total µg in plant	% uptake	root dry wt	root ash wt
1	0	1.0	1.3	7.3	9.6	-	6.94	0.91
2	0.98	2.8	5.8	74.4	83	8.5	15.35	1.86
3	1.95	1.7	1.3	112	115	5.9	9.00	1.25
4	3.9	1.1	2.1	175	178	4.6	7.43	0.50
5	7.8	5.1	3.0	750	758	9.7	13.40	1.50
6	15.6	5.3	5.7	720	733	4.7	7.25	0.80
7	23.5	5.4	12.4	780	798	3.4	7.10	0.68
8	31.2	9.8	21.6	3570	3601	11.6	16.21	2.75
9	46.9	5.7	44.8	1810	1861	4.0	7.70	1.10
10	62.5	17.5	25.7	2760	2803	4.5	12.00	1.20
11	95.0	14.4	24.8	5270	5309	5.6	12.58	1.51
12	125.0	37.4	22.5	8120	8180	6.5	13.03	1.89
13	250.0	52.7	68.8	7320	7441	2.9	10.63	1.22

Table II.5

Data for percentage distribution of tungsten

Plant no.	W in soil (ppm)	% in leaves	% in stems	% in roots
1	2.0	12.0	15.1	72.9
2	2.9	3.3	7.0	89.7
3	3.9	1.5	1.1	97.4
4	6.4	0.6	0.7	98.7
5	9.4	0.7	0.4	98.9
6	18	0.7	0.8	98.5
7	22	0.7	1.2	98.1
8	35	0.3	0.6	99.1
9	44	0.3	2.4	97.3
10	82	0.6	0.9	98.5
11	102	0.3	0.5	99.2
12	127	0.5	0.3	99.2
13	272	0.7	0.9	98.4
AVERAGE OF Nos. 3-13		0.6	0.7	98.7

originally present represents a large proportion of the total, the plants show a striking similarity in the way the tungsten is distributed between the leaves, stems and roots. Plant 9 differed from the other twelve in being considerably larger (height 54 cm, see Appendix 1) but had only a light leaf cover, and this probably explains its higher percentage of tungsten in the stems.

C. CONCLUSIONS

The results of these pot trials fulfilled their aims, and allowed the following conclusions to be made:

1. Tungsten added to the soil in the form of tungstate, can be taken up by plants in significant quantities.

2. The large amount of tungsten in the roots relative to the aerial parts of the plants is probably due partly to the addition of the tungsten in a soluble form over a short period, and partly to the ability of the plant to suppress translocation of this element.

3. In plants of similar size and age, grown in the same soil under identical conditions, the distribution of tungsten between the various plant organs is very consistent, and the concentrations of this element in the roots, stems and leaves are all related to the level of tungsten in the soil. The relationships were more significant on a ash-weight than on a dry-weight basis. This suggests that ash weight data is preferable in biogeochemical prospecting for tungsten.

4. The concentrations, of tungsten in the stems, and possibly in the roots, shows signs of reaching a limiting value over the range of tungsten used in the soil. However this tungsten is virtually all available to the plant whereas in the area of mineralisation where the element would be present mainly as calcium tungstate, only

a small proportion of the total would be available to the plant through weathering at any one time (c.f. control plant). Hence far higher soil tungsten concentrations than those used in the pot trials would be required to produce the same concentrations in the plants.

5. The total tungsten taken up, as a percentage of that added, shows a significant relationship with the root weight, indicating that the greater the volume of soil reached by the roots, the greater the amount of tungsten absorbed. This suggests a passive uptake, rather than active uptake in response to the plant's growth requirements.

6. The ability of the plants to survive, while containing up to 0.07% tungsten dry weight, seems to imply, in view of the reported inhibiting effect of tungstate on nitrate reduction, that the plants can obtain reduced nitrogen from other sources. There may be sufficient ammonium present in the potting mixture from the breakdown of humus. On the other hand, the roots of many New Zealand Podocarp species are known to contain mycorrhizal fungi which make reduced ammonia available to the plant (Baylis, McNabb and Morrison, 1963), and several Coprosma species show bacteria - containing stipular nodules which may function in the fixation of atmospheric nitrogen (Stevenson, 1953). It is possible therefore, that in the presence of high soil tungsten, and in the absence of sufficient soil ammonium ion, the plants may attain their requirements in one of these ways.

The results of these pot trials have provided much information, which was to be very useful in interpreting the field work described in the next Section, where the plant-soil relationship was complicated by many factors, such as the presence of many species of trees, variation in the pH of the soil, and the presence of the ore bodies.

SECTION III

GEOCHEMICAL AND BIOGEOCHEMICAL STUDIES OF TUNGSTEN AT BARRYTOWN

A. PRELIMINARY INVESTIGATION

1. Introduction

There is very little published work in existence dealing with biogeochemical exploration for tungsten. Palmquist and Brundin used this technique in the late 1930's, finding anomalous concentrations of this element in the leaves of trees and shrubs growing in high tungsten soils in Cornwall, England. However, little of their work was published, apart from a procedure describing the sampling and analytical technique used (Brundin, 1939).

In later years, several Russian workers referred to the possibility of using biogeochemical exploration for tungsten (Vinogradov, 1954; Malyuga, 1963; Kabiashvili, 1964), but to the author's knowledge it was not until 1966 that an actual investigation was carried out (Kovalevsky, 1966).

Like Palmquist and Brundin had done, Kovalevsky determined tungsten in soils and plants by semiquantitative emission spectrography, and reported a detection limit of 30 ppm in plant ash. This allowed for the detection of tungsten in only 210 of the 720 plant samples collected from the mineralised area, but did nevertheless provide much information.

The tungsten mineralisation in the area studied by Kovalevsky was represented by hubnerite ($MnWO_4$) and scheelite ($CaWO_4$) in variable proportions. The soil of the area was of the frozen forest type, with a pH of 4.0 to 4.5. The vegetation consisted mainly of pine, birch and sedge species.

Kovalevsky found that tungsten concentrations were highest in the roots, slightly lower in the trunk and branches (1500 ppm maximum), and lowest in the leaves, needles and twigs of trees and shrubs. He found that the tungsten concentrations in the plants did not correlate well with those in the soil, and assumed this to be caused by the irregular distribution of tungsten in the soil profile. However, the highest concentrations of tungsten

in the woody parts of Pinus sibirica were found in trees growing over tungsten-bearing veins and veinlets.

He concluded that branches and trunks should be sampled, rather than leaves, and that sampling points should be no more than 5 - 10 m apart to avoid missing individual ore bodies.

The results of Kovalevsky's work, together with the results of the tungsten uptake study described in Section II of this thesis, indicated that there was a potential use for biogeochemical prospecting for tungsten. With the permission and extensive assistance of Carpentaria Exploration Ltd. an investigation was therefore carried out in an area of tungsten mineralisation near Barrytown in Westland. The results of this investigation are described in this section.

The area, the geology and mineralisation of which are briefly described in the General Introduction, is shown in Fig. 0.1 and in more detail in Fig. III.0.

At the outset of this investigation, very little information was available concerning the mineralisation of the area. Tungsten mineralisation was thought to be represented mainly by scheelite, with some wolframite, in association with quartz veins, but the scarcity of outcrops prevented the tracing of these veins. Associated mineralisation included small amounts of arsenopyrites and tourmaline.

The soil was composed of a dark-brown humus - rich A horizon approximately 0.3 m deep overlying a lighter brown B horizon which varied enormously in thickness because of the presence of landslide debris in many areas. The pH of the soil was low but variable, the few samples determined ranging from 4.0 to 6.2 compared to the relatively small range of 4.0 to 4.5 in the area in Russia studied by Kovalevsky.

Vegetation was represented mainly by Nothofagus truncata (hard beech) and Weimannia racemosa (kamahi),

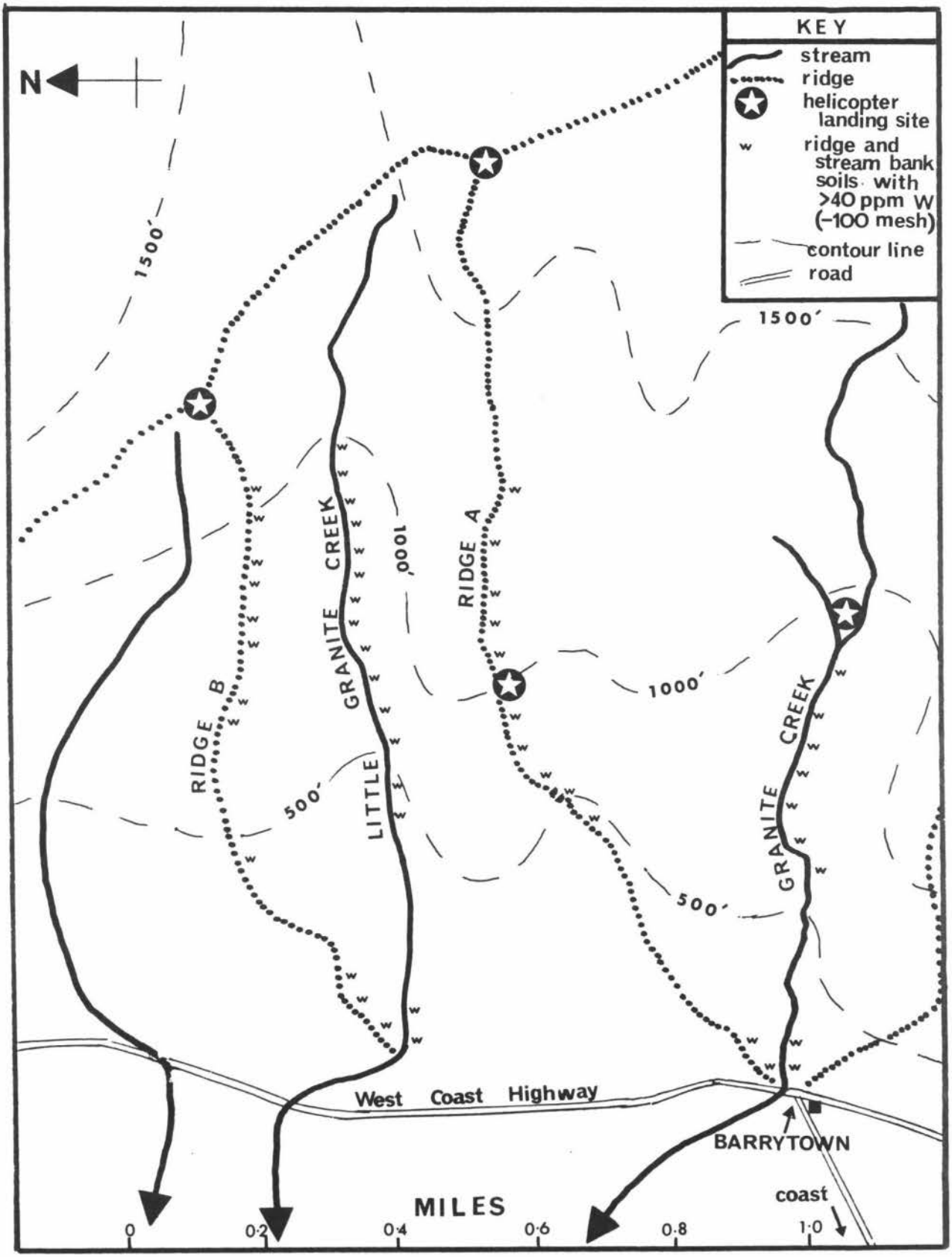


Fig. III.0. Map showing Barrytown study area.

with increasing dominance of N. menziesii (silver beech) at higher altitudes. The beech species are well known for the acidic nature of their litter, and the reducing conditions resulting from this, in conjunction with the 110" rainfall, has produced a leached A_2 horizon in some of the flatter areas (caused by reduction of the ferric ion to ferrous).

The aim of this preliminary investigation was to determine whether any metals were associated with tungsten in the soil, and whether the tungsten concentration in any of the commoner plant species indicated the concentration of this element in the soil. By comparing the concentration of a number of major and trace metals in the various plant species, the feasibility of grouping any of the species together for the purposes of biogeochemical prospecting was assessed.

2. Sampling methods

(a) Sampling sites

Soil sampling had been carried out by Carpentaria Exploration Ltd. at 100' intervals up Ridges A and B and along the banks of Granite and Little Granite Creeks (Fig. III.0). Cuts of these samples (numbering 220) were kindly made available for analysis.

In order to determine whether the concentration of tungsten in the plants indicated that in the soil, it was decided to collect plant samples from near these soil sampling sites, to enable comparison of plant-soil data without the necessity of further time-consuming soil sampling.

(b) Species sampled

The criteria for selection of a particular plant species for this preliminary investigation were as follows:-

(i) That it be fairly evenly distributed over the area being investigated, and in sufficient numbers, so that samples could be obtained at as many of the existing soil sampling sites as possible;

(ii) That it be commonly found in areas of similar climatic and ecological environment, so that any conclusions made concerning its prospecting possibilities could be applied to these other areas.

As mentioned before, the predominant species on the ridges were Nothofagus truncata (hard beech), which tended to give way to N. menziesii (silver beech) at higher altitudes. Weimannia racemosa (kamahi) was also very much in evidence. Chief secondary species were Quintinia acutifolia and Myrsine salicina.

These five species were chosen for sampling. Leaves from four are shown in Plate III.1, together with leaves of a third beech species, N. fusca (red beech), which grew only in isolated pockets and was not found sufficiently near any of the soil sites to render sampling worthwhile.

The kamahi and beech species, with their low nutrient-requirements, are particularly well suited to poor-quality soils such as those over granite, which is very resistant to weathering and hence yields up its nutrients very slowly. As will be seen later, the soil is of even poorer quality on the ridge crests than down on the stream banks, due at least in part to the leaching produced by the 110" rainfall.

Another aspect which made beech a suitable tree to sample is the nature of its dispersal mechanism. Its seed, being very large, is not carried by birds, and wind does not carry it much further than the height of the tree. Also, beech seeds will in general germinate only in beech litter. Beech forests therefore advance very slowly and tend to do so as a wall of beech. It may be concluded then that, where beech is growing, the soil it is growing in will have been derived directly from bedrock formations rather than from miscellaneous alluvial or colluvial materials of uncertain origin. This conclusion applies to a lesser extent to the associated kamahi, plus possibly to the secondary species Q. acutifolia and M. salicina.

Finally, all the above-mentioned species are found

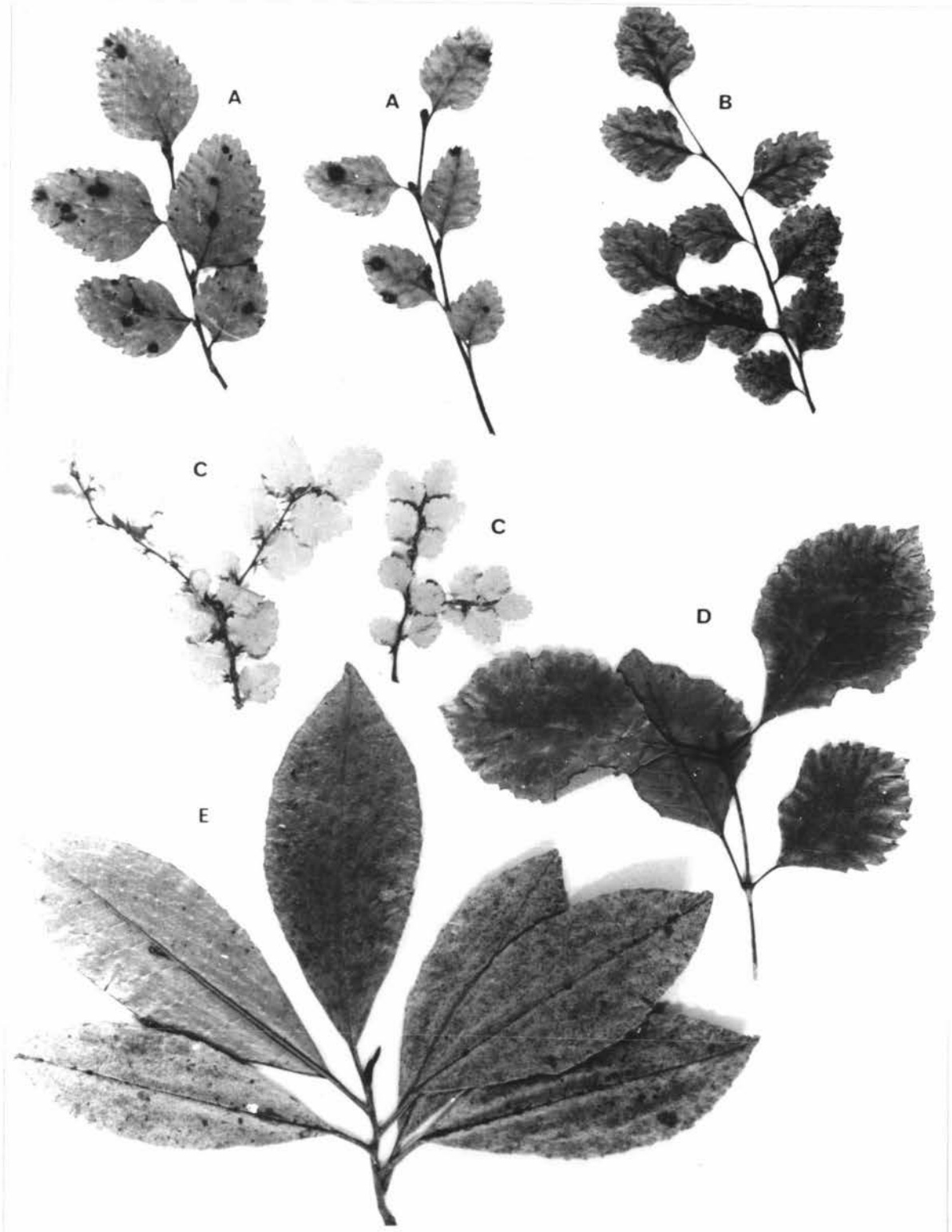


Plate III.I. Leaves from the trees sampled

A. Nothofagus truncata
B. N. Fusca
C. N. menziesii
D. Weimannia racemosa
E. Quintinia acutifolia

widely in New Zealand, particularly in the South Island.

The vegetation of the stream banks was much more diverse, including in addition to the above species many Coprosmas and Podocarps and tree ferns, particularly Cyathea medullaris (king fern) and Dicksonia squarrosa (wheki). However because only the tree ferns were found growing near most of the soil sites, the forest trees being found in general further up the bank, it was decided to sample only the tree ferns. (A small number of the other species were sampled to compare their metal content with those on the ridges).

On both ridges and stream banks, plant samples were taken only if the chosen species were growing within 3 m of the soil site, in order to reduce the error resulting from fluctuations in soil tungsten with distance.

(c) Plant organs sampled

The criteria for selection of a particular plant organ for sampling were:

(i) That it be easily and rapidly sampled,

(ii) That its removal did not unduly harm the plant.

Samples of the trunks, twigs and leaves of ridge trees were taken.

Trunk samples were most easily taken with a machete, a slice being cut from the outer trunk at chest height, at depths up to 2 cm, after removing the bark. No trunk samples were taken from the secondary species Quintinia acutifolia or Myrsine salicina because of the small size of these trees (average trunk diameter 6 - 8 cm).

Twig samples were kept to roughly uniform size, about 1 cm diameter, and were taken from various points on the tree to ensure a representative sample.

Leaves were also taken from various points on the tree, and both new and old leaves were sampled.

Due to the height of the beech trees, few samples of leaves and twigs were obtained from them. Although more

could have been obtained by using a loop or cutting instrument on a long pole, the rugged topography of the area would have made this method of collection difficult and slow.

The tree ferns on the stream banks were sampled by removing portions of fronds from different points on the plant.

The plant samples, generally weighing about 200 g, were stored in plastic bags sealed with rubber bands for transportation to the laboratory. On arrival they were dried at 110°C in paper bags and stored in this form until they were analysed.

3. Analytical methods

(a) Soils

Soil samples were air-dried before the -100 mesh fraction was removed by dry-sieving. This fraction was then analysed for the following metals:

(i) Tungsten

Tungsten was analysed by the colorimetric procedure developed in Section I.C of this thesis. Some soils were also analysed for tungsten by emission spectrography (Section I.B). The results by the two methods correlated well and are shown in Fig. III. 1.

(ii) Molybdenum and tin

Some of the soils were analysed for molybdenum and tin by emission spectrography, using the conditions shown in Table I.4.

(iii) Other metals

Strontium, manganese, zinc, copper, nickel, lead and iron in soils were determined by atomic absorption spectrophotometry using a Techtron AA5 model with air-acetylene flame. The sample (0.2 g) was taken down to dryness with 10 cm^3 of a one to one mixture of nitric and hydrofluoric acids in polypropylene beakers over a boiling water-bath. Approximately 7 cm^3 of 2N hydrochloric acid were

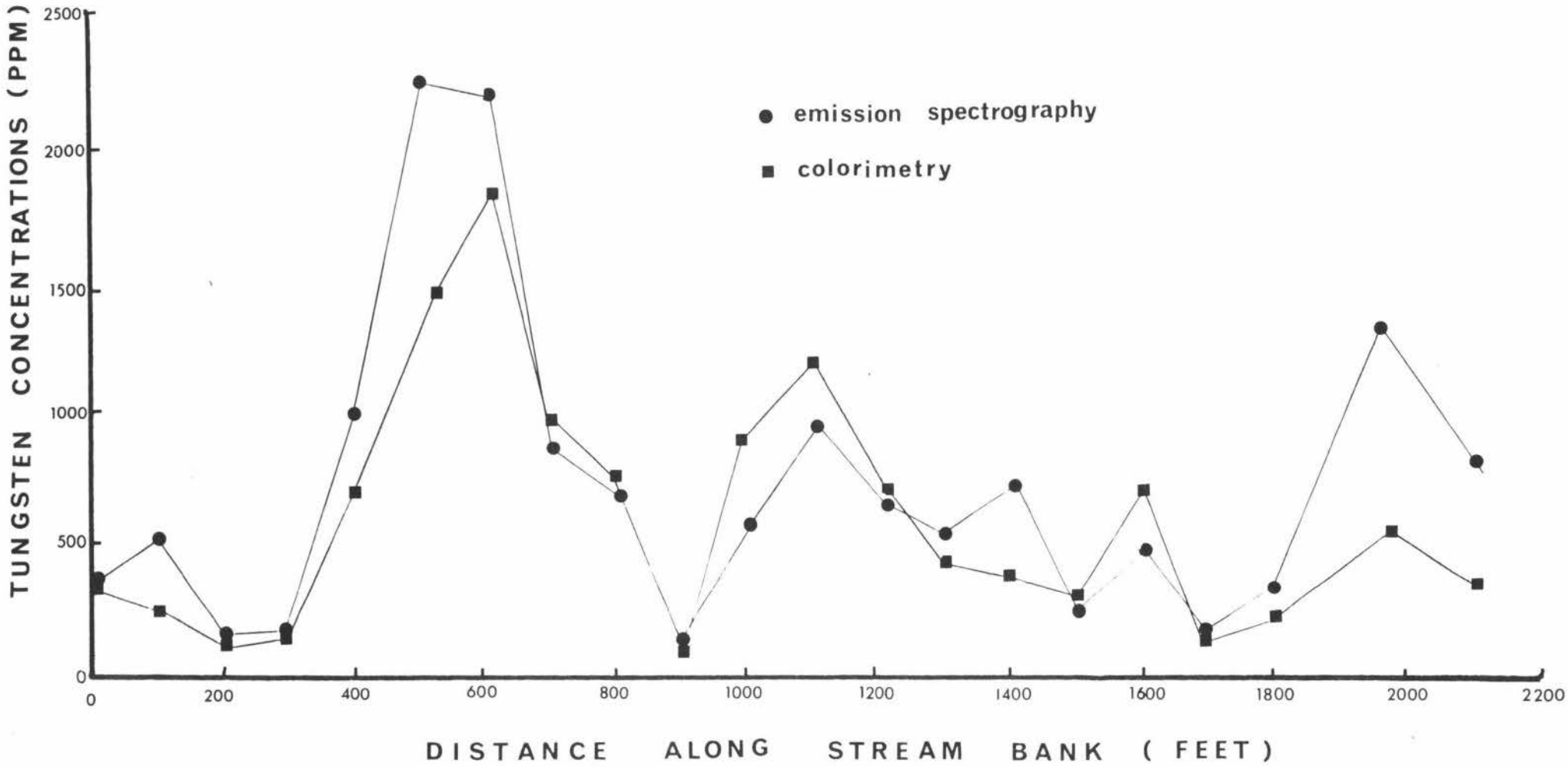


Fig. III.I. Comparison of tungsten analyses by emission spectrography and colorimetry.

then added to dissolve the residue. After continued heating had reduced the sample volume to 3-5 cm^3, the supernatant liquid was transferred to a test-tube and made up to 10 cm^3, making a 50 times dilution. The solution as such was analysed for Sr, Mn, Zn, Pb, Cu and Ni.

Before analysing for iron, 50 μl of this solution was diluted to 2 cm^3 with 2N hydrochloric acid, making a 2000- fold dilution overall.

(b) Plants

Samples of leaves and twigs were washed thoroughly in running water, to remove possible soil and dust contamination. The covering of bark made this unnecessary for trunk samples. In any case, the lack of exposed soil, dense vegetation canopy and relatively high rainfall would effectively prevent severe contanination. The plant samples were dried at 110°C, then dry ashed at 450°C before being analysed for the following metals:

(i) Tungsten

Tungsten in plant ash was determined using the colorimetric procedure developed in Section I.C of this thesis.

(ii) Other metals

Strontium, manganese, zinc, copper, lead, iron, calcium and magnesium in plant ash were determined by atomic absorption spectrophotometry, using a Techtron AA5 model with air-acetylene flame. The sample (0.1 g) was dissolved in 10 cm^3 of 2N hydrochloric acid (making a 100-fold dilution) by heating in a boiling water bath for 20 minutes. The solution was analysed for Sr, Mn, Zn, Cu, Pb and Fe once the residue, if any, had settled.

Before analysing for calcium and magnesium, a further 50- fold dilution was carried out with 2N hydrochloric acid containing 0.8% strontium nitrate, which prevents the phosphate present in the sample from interfering with their determination.

(c) General

In general, mixed standards covering the range

0-20 ppm in solution were used, and analysis was carried out using the absorption mode so that it was not necessary to draw standard curves. The conditions used for the atomic absorption analysis of soil and plant samples are shown in Table III. 1. For the metals analysed, a reproducibility of $\pm$ 10% was achieved, and Table III.2 shows the results of six replicate analyses of a tree fern sample.

4. Statistical treatment of data

(a) Cumulative frequency plots

Cumulative frequency studies of some of the soil data were carried out. A plot of the cumulative frequency of the concentrations of the samples, as a percentage of the total number of samples, plotted on probability paper against the concentration value, has been shown to be useful for geochemical data interpretation (Tennant and White, 1959; Williams, 1967). In particular, log- normal distributions will show a straight line when plotted on log- probability paper. In other cases, curves will ensue, for example when the data are normally distributed. However, if there is more than one distribution set within the data, such as could occur in mineralised and unmineralised soil samples, a distinct change of slope or a point of inflexion in the graph will be observed. This break may be considered to occur near the minimum concentration of mineralised samples, although some overlap of distributions will occur (Williams, 1967). Generally, however, cumulative frequency graphs show the presence of more than one distribution more clearly than do histograms, especially if the distribution due to mineralisation contains a far smaller number of samples than does the unmineralised distribution.

(b) Correlation coefficients

As a preliminary device for scanning large quantities of data, Pearson Product Moment correlation coefficients were calculated by computer. This particular coefficient is quite sensitive to the distribution of data sets, requiring normally distributed data for complete mathematical

Table III.1

Analysis conditions for atomic absorption spectrometry

Metal	Wavelength (Å)	Slit width (Å)
Strontium	4607.3	3.3
Manganese	2794.8	3.3
Zinc	2138.6	3.3
Copper	3247.5	3.3
Lead	2170.0	6.6
Nickel	2320.0	3.3
Iron	2483.3	3.3
Calcium	4226.7	3.3
Magnesium	2852.1	3.3

Table III.2

Results for replicate atomic absorption analysis of a tree-fern sample

Number	Sr ppm	Mn ppm	Zn ppm	Cu ppm	Pb ppm	Fe ppm	Ca %	Mg %
1	55	1000	600	550	25	1120	3.4	5.0
2	60	1000	600	550	25	1120	3.4	5.2
3	60	900	560	510	20	1050	3.1	4.8
4	60	950	590	540	30	1080	3.2	5.0
5	75	950	590	550	30	1100	3.4	5.0
6	60	950	580	520	30	1060	3.2	5.0

validity. Norris and Hjelm (1961) have tested the "robustness" of the correlation when applied to non-normal data, and found that, in general, if the data distributions did not depart too far from normality, then the resulting coefficient was quite valid.

With most geochemical data, badly skewed distributions are the rule, rather than the exception, the data in general being closer to a log-normal distribution (Ahrens, 1954). By converting the data to base ten logarithms before computation of the correlation coefficients, the problem of skewness is therefore largely overcome.

The computer programme used was written by M.H. Timperley for use on an IBM 1620 II computer (Timperley, 1971). Levels of significance used in this thesis were taken from the tables of Fisher and Yates (1957).

5. Results and discussion

(a) Analytical data

(i) Soils

Analytical data for soil samples are given in Table III.3.

The concentrations of tungsten, iron, manganese and zinc, and to a lesser extent lead and strontium are seen to be considerably lower in the soils from the ridges than in those from the stream banks. Although the difference in the tungsten concentrations must be due at least in part to the fact that most of the outcrops of tungsten-bearing veins are near streams rather than on ridges, the differences for the other five metals are most likely caused by the leaching produced by the high rainfall, as all these metals can exist in soluble forms under reducing conditions. This is particularly true for iron and manganese, which are converted to soluble Fe (II) and Mn (II) species respectively in a reducing environment of low pH, while zinc is usually soluble. Lead and strontium may become precipitated as their slightly soluble sulphates in reducing conditions (Rankama and Sahama, 1950) and this

Table III.3

Analytical data for soils

Locality	No. of samples		W ppm	Mo ppm	Sn+ ppm	Sr ppm	Mn ppm	Zn ppm	Cu ppm	Ni+ ppm	Pb ppm	Fe %
Stream banks	94	min	4	1	4	2	60	30	8	10	15	0.5
		max	1800	27	105	490	1900	275	61	38	120	6.5
		mean	98	5.6	30	20	400	88	23	23	60	3.5
Ridges	124	min	3	-	6	5	40	10	5	7	15	0.1
		max	620	-	80	145	460	140	150	40	135	3.6
		mean	44	-	29	15	95	46	25	25	40	1.9

+Data for Sn and Ni in Ridge soils represent 25 samples only.

N.B. Means are geometric, not arithmetic.

may explain why their mean stream-bank and ridge concentrations are more similar.

Copper and nickel, on the other hand, tend to form insoluble sulphides in reducing conditions if sulphide is present. In this area sulphide is present, as arseno-pyrites, and the resultant lack of leaching of these two metals would explain their similar concentrations in stream-bank and ridge soils.

Finally tin, in the form of cassitorite, the commonest of tin minerals, is very resistant to weathering, and the tin originally found within other minerals and silicate rocks is also promptly precipitated after the decomposition of the minerals in question (Rankama and Sahama, 1950). Similar tin concentrations in ridge and stream-bank soils are therefore not unexpected.

(ii) Tree data

General

An outstanding feature of the data for trees (Table III.4) is the differences that exist between the concentrations in the different species, not only of the trace metals bur also of the major nutrients.

As the plant samples were collected at the same group of soil sites, these observed differences between species are too great to be due solely to varying soil concentrations, except in the case of tungsten, which showed a wider range of concentration in the soil than any of the other elements analysed.

The results also illustrate the different ways in which metals are distributed between the leaves, twigs and trunks of a particular sample. For example, the concentration of copper in the twigs of Quintinia acutifolia and Weimannia racemosa are similar, and are approximately twice as high as the concentration of this element in their leaves. In Myrsine salicina however, the copper concentration is lower in the twigs than in the leaves.

When the two beech species are compared, it is seen that the concentrations of the various metals in their trunks

Table III.4

Analytical data for trees

Species & organ	No. of samples		W ppm	Sr ppm	Mn %	Zn ppm	Cu ppm	Pb ppm	Fe %	Ca %	Mg %	Ash %
N.menziesii												
		min.	0.5	500	0.48	640	130	30	0.15	18.0	2.2	2.3
leaves	6	max.	7	1400	1.1	1300	330	60	0.26	25.0	4.7	4.0
		mean	2.2	850	0.76	910	195	45	0.19	20.0	3.3	3.5
		min.	0.6	550	0.36	490	100	20	0.05	12.0	1.6	1.7
twigs	5	max.	7	2100	0.81	850	140	40	1.0	30.0	2.2	2.5
		mean	1.3	1380	0.50	610	110	31	0.07	24.5	1.9	2.1
		min.	0.2	450	0.08	170	80	5	0.02	4.2	0.7	-
trunks	27	max.	275	1950	0.58	1160	380	110	0.10	16.5	3.1	-
		mean	8.4	940	0.25	540	185	16	0.06	7.9	1.7	-
M.truncata												
		min.	0.4	350	0.08	130	70	5	0.02	2.5	0.8	-
trunks	56	max.	300	3100	0.80	810	280	85	0.14	23.8	3.6	-
		mean	6.6	1190	0.21	280	130	15	0.05	8.4	1.7	-
W.racemosa												
		min.	0.4	200	0.46	190	70	20	0.06	16.0	6.2	3.9
leaves	40	max.	12	2350	2.29	600	250	140	0.20	33.0	25.0	8.3
		mean	2.2	810	1.03	275	105	42	0.10	23.7	10.1	4.8
		min.	<0.1	900	0.22	330	170	20	0.04	14.0	4.9	0.5
twigs	37	max.	13	2600	2.45	910	430	80	0.18	31.0	10.2	2.0
		mean	0.9	1800	0.93	510	280	41	0.09	21.6	6.5	1.3
		min.	0.6	450	0.07	120	55	5	0.02	6.5	1.5	-
trunks	79	max.	100	3200	1.10	1480	1450	80	0.12	30.5	12.0	-
		mean	5.8	1615	0.32	390	165	27	0.05	14.9	4.2	-
Q.acutifolia												
		min.	0.7	900	0.36	170	60	25	0.07	16.5	5.6	2.4
leaves	30	max.	7	3400	2.41	330	160	190	0.13	27.5	14.6	7.5
		mean	3.0	1670	0.95	225	92	100	0.09	21.2	8.8	5.7
		min.	<0.1	1600	0.20	190	130	20	0.03	16.0	2.4	0.69
twigs	28	max.	15	3300	1.72	1280	330	165	0.09	38.0	7.5	2.3
		mean	0.7	2350	0.56	500	205	58	0.05	22.7	4.7	1.5
M.salicina												
		min.	<0.1	75	0.02	120	60	25	0.04	12.0	3.0	5.7
leaves	42	max.	50	2675	0.25	270	140	120	0.09	29.0	9.0	8.3
		mean	2.8	725	0.08	170	87	86	0.06	18.4	5.6	6.8
		min.	0.1	1100	0.02	40	50	5	0.02	13.0	0.8	1.8
twigs	41	max.	24	5000	0.18	250	300	170	0.08	38.0	4.9	4.9
		mean	0.2	3100	0.06	130	120	42	0.04	27.6	2.4	2.6

N.B. Means are geometric, not arithmetic.

are very similar, with the notable exception of zinc, which is approximately twice as high in Nothofagus menziesii (silver beech) as in N. truncata (hard beech). This zinc difference has also been found to be the case for beech leaves by Timperley (1971), who also found that N. menziesii has a higher concentration of chromium (not analysed for in this study). Because of the similarities in the metal contents of these two species, it is likely that they could be treated as one species in biogeochemical prospecting.

Tungsten

The results for all the tree species (Table III.4) show that the mean tungsten concentration decreases in the order

trunks > leaves > twigs

Kovalevsky (1966) also found that the trunks (and branches) contained higher concentrations of tungsten than the leaves or twigs, and found that, for most species, the concentration in the twigs tended to reach a limiting value while the concentration in the leaves was still increasing.

In the uptake experiment described in Section II of this thesis, it was found that the concentration of tungsten in the stems tended to reach a limiting value, although the concentration in the leaves increased constantly over the range attained in the experiment.

This suggests that the stems of these three-year-old plants were behaving physiologically more similarly to the twigs than to the trunks of older trees.

Tungsten was detected in 348 (90%) of the 390 tree samples analysed. Those that were below the detection limit of 0.1 ppm (ash weight) were all twig samples. This indicates that in unmineralised areas, the average concentration of tungsten in at least the twigs of trees would be less than 0.1 ppm (ash weight).

(iii) Tree fern data

General

The most outstanding feature of these results (Table III.5) is that unlike in the tree leaves where the calcium concentration is greater than the magnesium concentration, the concentration of calcium in the tree ferns is less than that of magnesium, particularly in the less advanced Dicksonia squarrosa, suggesting that a low Ca/Mg ratio may be connected in some way with the relatively primitive physiology of the tree ferns. The ferns also exhibit a much lower strontium concentration than do the trees.

The concentration of all the metals analysed are lower in D. squarrosa than in C. medullaris. Because of the slightly lower ash percentage of the former species, this difference would be slightly less significant on a dry-weight basis.

Tungsten

The range of tungsten concentrations in the two species is similar, suggesting that the species do not differ markedly in their response to tungsten in the soil.

(b) Cumulative frequency plots

Cumulative frequency studies were carried out on soil data for tungsten, manganese, lead, tin, iron, molybdenum, zinc, copper and nickel.

Because of the differences in the mean concentration of some elements in ridge and stream-bank soils (Table III.3), the effect this could have on the cumulative frequency plots was investigated, by comparing plots for the total data with those for ridge and stream-bank data plotted separately. (Fig. III.2).

(i) Tungsten

The plot for the total data indicates the presence of two distributions (Fig. III.2(a)). As the stream-bank and ridge soil data taken separately also show two distributions

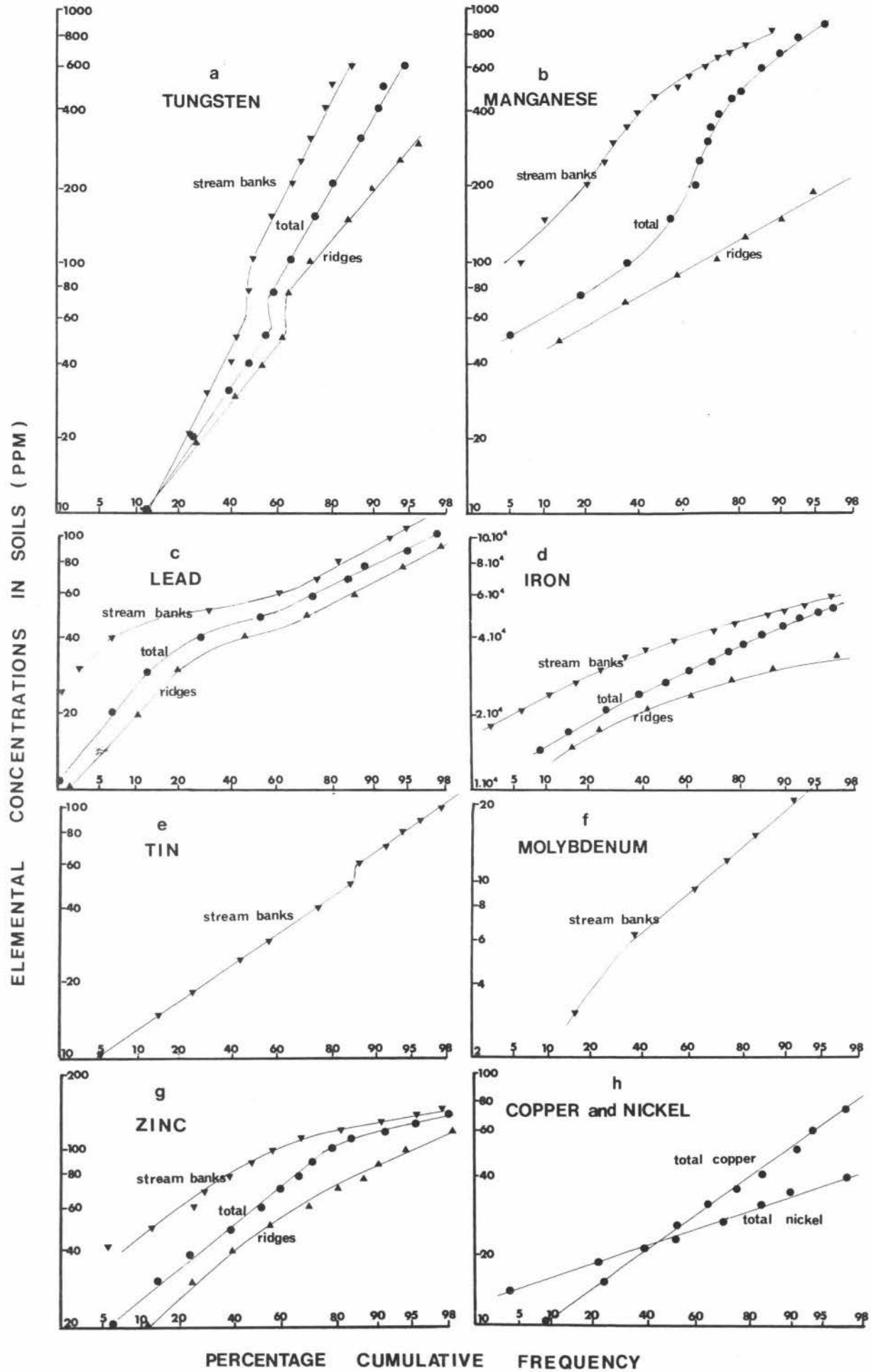


Fig. III.2. Cumulative frequency plots for soil data.

Table III.5

Analytical data for tree-fern leaves

Species	No. of samples		W ppm	Sr ppm	Mn %	Zn ppm	Cu ppm	Pb ppm	Fe %	Ca %	Mg %	Ash %
Cyathea medullaris	65	Min.	0.2	10	0.04	120	30	10	0.04	1.1	1.2	4.3
		max.	85	500	0.70	780	1000	110	0.27	7.9	5.8	8.6
		mean	7.3	140	0.23	430	210	31	0.13	3.3	3.5	5.9
Dicksonia squarrosa	12	min.	3.0	70	0.12	130	70	5	0.06	0.9	1.9	3.7
		max.	60	200	0.24	450	330	30	0.13	2.3	4.0	7.3
		mean	5.6	120	0.16	290	165	18	0.09	1.4	2.6	5.6

N.B. Means are geometric, not arithmetic

(Fig. III.2(a)), this indicates that the upper distribution is in fact due to mineralisation, the lower distribution representing the barren rock.

(ii) Manganese

When the total data are plotted, two distinct distributions are found (Fig. III.2(b)). Superficially, this suggests that the upper distribution is due to the presence of wolframite ($(Fe,Mn)WO_4$). When the stream-bank and ridge data are plotted separately (Fig. III.2(b)), while there still seems to be two distributions for the stream-bank data, there is no evidence of two distributions in the ridge data. This could be explained however if the manganese has been leached from the wolframite on the ridges and only some of the manganese derived from the more resistant granitic country rock remains in the soil.

(iii) Lead

The plot for the total lead data indicates the presence of two distributions. This is also shown when the ridge and stream-bank data are plotted separately (Fig. III.2(c)). Although this could be due to the presence of lead mineralisation of some sort, its presence has not been reported, and a more likely explanation is that Pb (II) can partially diadochically replace Ca(II) in calcium minerals such as scheelite (Rankama and Sahama, 1950). That this is the true explanation is supported by the fact that a sample of scheelite from the area was found to contain 190 ppm lead.

(iv) Tin

The plot for tin in stream-bank soils also indicates the presence of two distributions (Fig. III.2(e)). The upper distribution could be caused by the presence of small amounts of cassiterite (SnO_2), a mineral often associated with tungsten deposits. In addition, tin (IV) can replace tungsten in its ores, and wolframite, for example, may contain up to 1% tin (Otteman, 1941). That replacement is at least partially responsible for the second tin

distribution is supported by the fact that a sample of scheelite from the area was found to contain approximately 300 ppm tin. Too few data were available for ridge soils to permit cumulative frequency studies, but the similarity of the mean tin concentrations in ridge and stream-bank soils (Table III.3) indicates that its distribution would be the same in both cases.

(v) Iron

The data for iron show only one distribution whether they are plotted for all soils or for stream-bank and ridge soils separately (Fig. III.2(d)). Because the iron present in the wolframite is so small compared to the amount derived by weathering of the granite, it does not show up as a second distribution. This would probably also be the case for calcium, the calcium from the scheelite being but a small proportion of the total present.

(vi) Molybdenum

The plot for the stream-bank data (Fig. III.2(f)) shows the presence of only one distribution, indicating that molybdenum is present only in the granitic country rock and not as mineralisation.

(vii) Zinc

The plot for the total zinc data shows a slight indication of two distributions. However when the stream-bank and ridge data are plotted separately (Fig. III.2(g)), it is evident that only one distribution is present, the levelling of the curve being caused by the data being closer to a normal than a log-normal distribution.

(viii) Copper and nickel

Both these elements show single log-normal distributions when the total data for each are plotted (Fig. III.2 (h)). . . This is in line with the similar means for ridge and stream-bank soils and with the absence of minerals of these two elements.

Of the elements investigated, tungsten, manganese tin and lead indicate the presence of two distributions. Normal background levels of manganese in soils are considerably higher than those at Barrytown, and it is likely that they would usually be high enough to mask a second distribution due to mineralisation, as was the case for iron.

(c) Correlation Coefficients

Correlation coefficients were first calculated between tungsten and the other elements analysed in the soils, to determine if any relationships existed and to indicate whether these related elements could be useful pathfinders for tungsten.

Secondly, correlation coefficients were calculated between tungsten in the soil and in the various plant species, to determine if the concentration of tungsten in any of these species could be used to predict the concentration of this element in the soil.

(i) Inter-soil correlations

Because of the differences in the mean concentrations of some elements in stream-bank and ridge soils (Table III.3), and the problems this could cause in statistical analysis (Fig. III.2), the two groups of data were kept separate for the determination of correlation coefficients.

Stream-bank soils

The results for the stream-bank soils are given in Table III. 6. Very highly significant correlations were found to exist between tungsten and manganese, lead and tin. The data for these three correlations are plotted in Fig. III.3. Correlations of tungsten with all the other elements were not significant.

These results are supported by the cumulative frequency plots (Fig. III.2) as, besides tungsten, only the three elements Mn, Pb and Sn indicate the presence of two distributions. The higher distribution in each case must be responsible for the very highly significant correlation with tungsten.

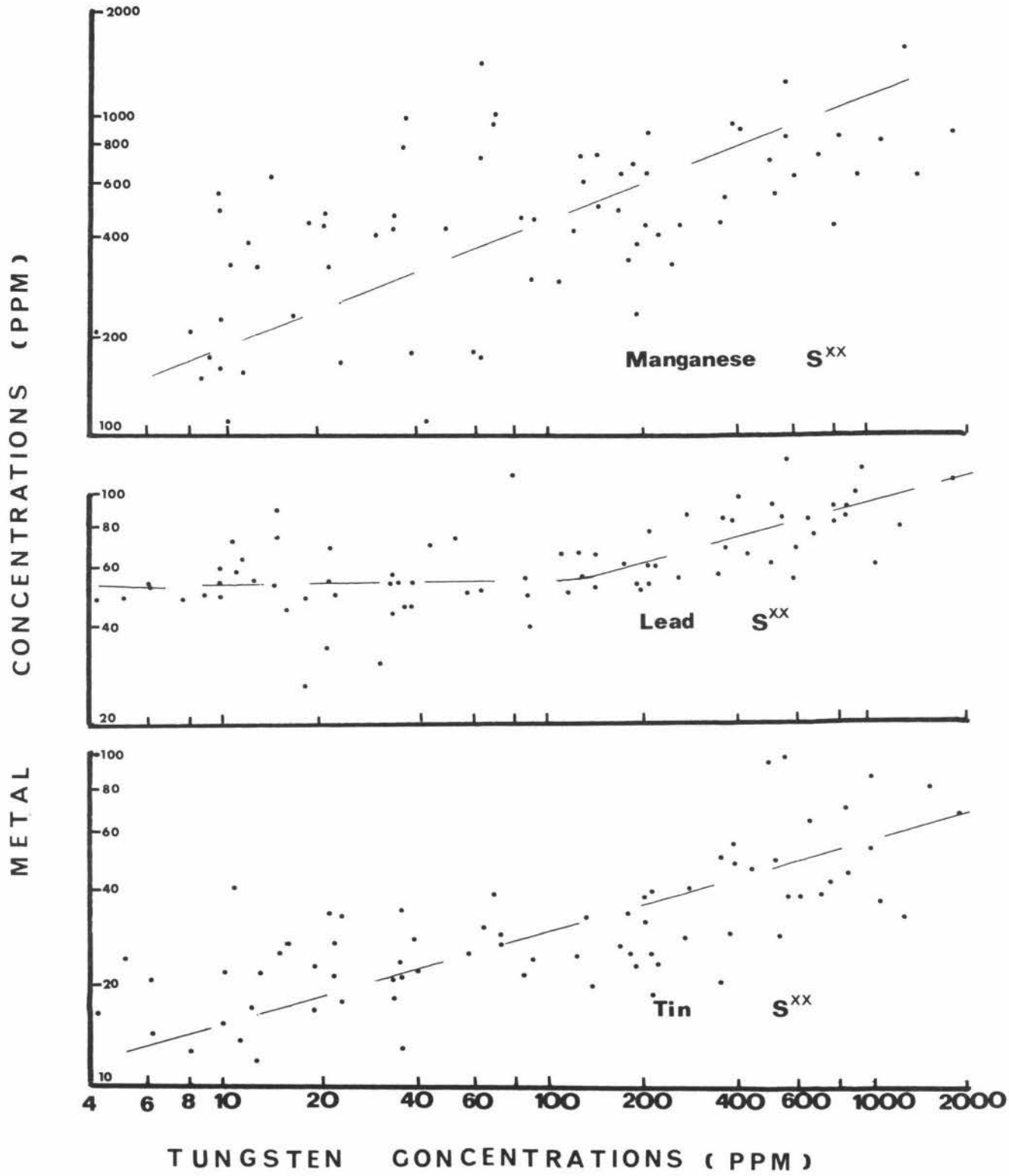


Fig. III.3. Variation of tungsten in stream–bank soils with manganese, lead and tin.

Ridge soils

The results for the stream-bank soils also show very highly significant correlations between tungsten and tin, and tungsten and lead (Table III.6). However the correlation between tungsten and manganese was not significant, probably because of the extensive leaching of manganese from the ridge soils. As mentioned earlier, lead is less mobile under reducing conditions, and tin is particularly resistant to weathering. The existence of very highly significant relationships between tungsten and lead and tungsten and tin, but not tungsten and manganese, suggests that tungsten is also relatively immobile in reducing conditions. The data for the three correlations are plotted in Fig. III.4.

Discussion

The correlation results suggest that manganese, lead and tin could be useful pathfinders for tungsten, although the greater mobility and normally higher concentrations of manganese pose problems. To be worthwhile, a pathfinding element should, because of some particular property or properties, provide anomalies or dispersion halos more readily useable than the sought-after element with which they are associated. To establish definitely whether Mn, Pb and Sn achieve this aim would require rather more work than the scope and length of this thesis permits, but this preliminary study carried out has succeeded in demonstrating that this possibility exists.

A further element which may be of potential use as a pathfinder for tungsten is arsenic, because of the presence of arsenopyrites in association with the tungsten mineralisation. Because of the time that would have been involved in developing a reliable analysis procedure, this was not investigated in this work.

Table III.6

Correlation results for soil data

Correlation	Significance	
	Stream-bank soils	Ridge soils
W - Mn	S^{++}	NS
W - Pb	S^{++}	S^{++}
W - Sn	S^{++}	S^{++}
W - Fe	NS	NS
W - Mo	NS	NS
W - Zn	NS	NS
W - Cu	NS	NS
W - Ni	NS	NS

Levels of significance (Brookes, Betteley, and Loxston, 1966) shown above are as follows:

S^{++}	(very highly significant) : significant at 0.1% level
S^{+}	(highly significant) : significant at 0.1 - 1% level
S	(significant) : significant at 1 - 5% level
PS	(possibly significant) : significant at 5 - 10% level
NS	not significant.

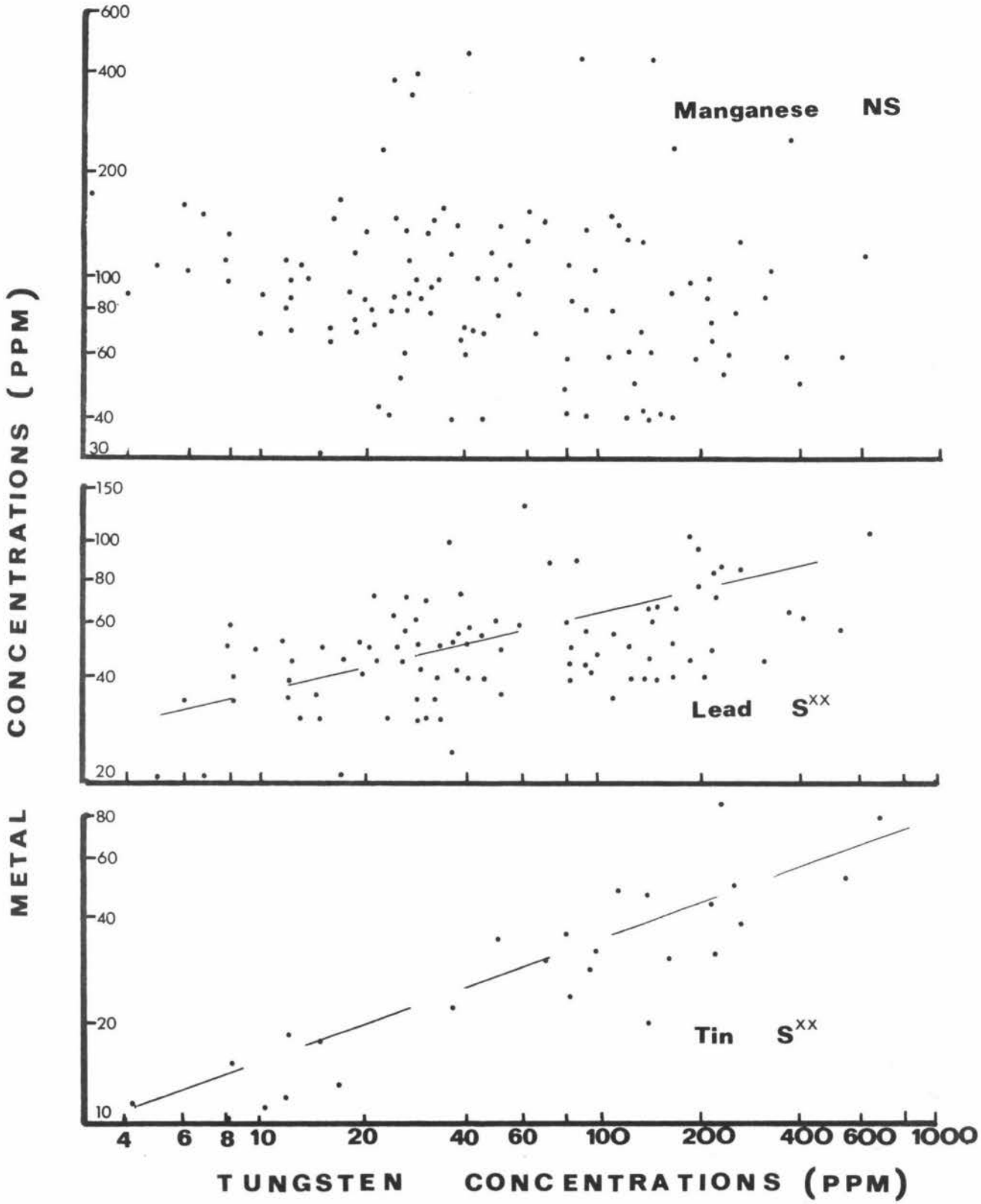


Fig. III.4. Variation of tungsten in ridge soils with managanese, lead and tin.

(ii) Plant - soil correlations

Correlations were calculated on both ash and dry-weight bases for plants, to examine whether one is markedly superior to the other for biogeochemical prospecting purposes.

Stream-bank tree-ferns

The tungsten concentration in the tree fern leaves showed a very highly significant correlation (both on ash and dry-weight bases) with that in the soil. (Table III.7). The data are plotted in Fig. III.5 (a) and are shown as a profile in Fig. III. 5(b). The significance of the correlation was the same whether the two tree-fern species were taken together or separately, and for this reason the data are plotted together.

Ridge trees

No very highly significant correlations were found between tungsten in any of the tree organs and that in the soil (Table III.7). However significant correlations were found for Quintinia acutifolia twigs and Myrsine salicina leaves on both ash and dry-weight bases. The data are plotted in Fig. III.6(a) and are shown as profiles in Fig. III.6(b). As trunks of these species were not sampled, it could not be established whether they would have given a more significant correlation.

No significant correlations were found for any of the organs of the beech species or kamahi, although the numbers of beech leaves and twigs were too small for an accurate correlation coefficient to be determined.

Discussion

The ability of the vegetation to predict the tungsten concentration in the soil decreases in the order

tree ferns > small trees > large trees

A possible explanation for this order is as follows. Tree ferns have a shallow and localised root system, and they would therefore take up most of their minerals from the

Table III.7

Correlation results for tungsten in plants and soils

Plant species	Plant organ	Correlation significance
Cyathea medullaris, *Dicksonia squarrosa*	leaves	S^{++}
Nothofagus menziesii	leaves	(NS)[a]
	twigs	(NS)[a]
	trunks	NS
Nothofagus truncata	trunks	NS
Weinmannia racemosa	leaves	NS
	twigs	NS
	trunks	NS
Quintinia acutifolia	leaves	NS
	twigs	S
Myrsine salicina	leaves	S
	twigs	NS

[a]Sample numbers too small for accurate determination of correlation.
Levels of significance as for Table III.6.

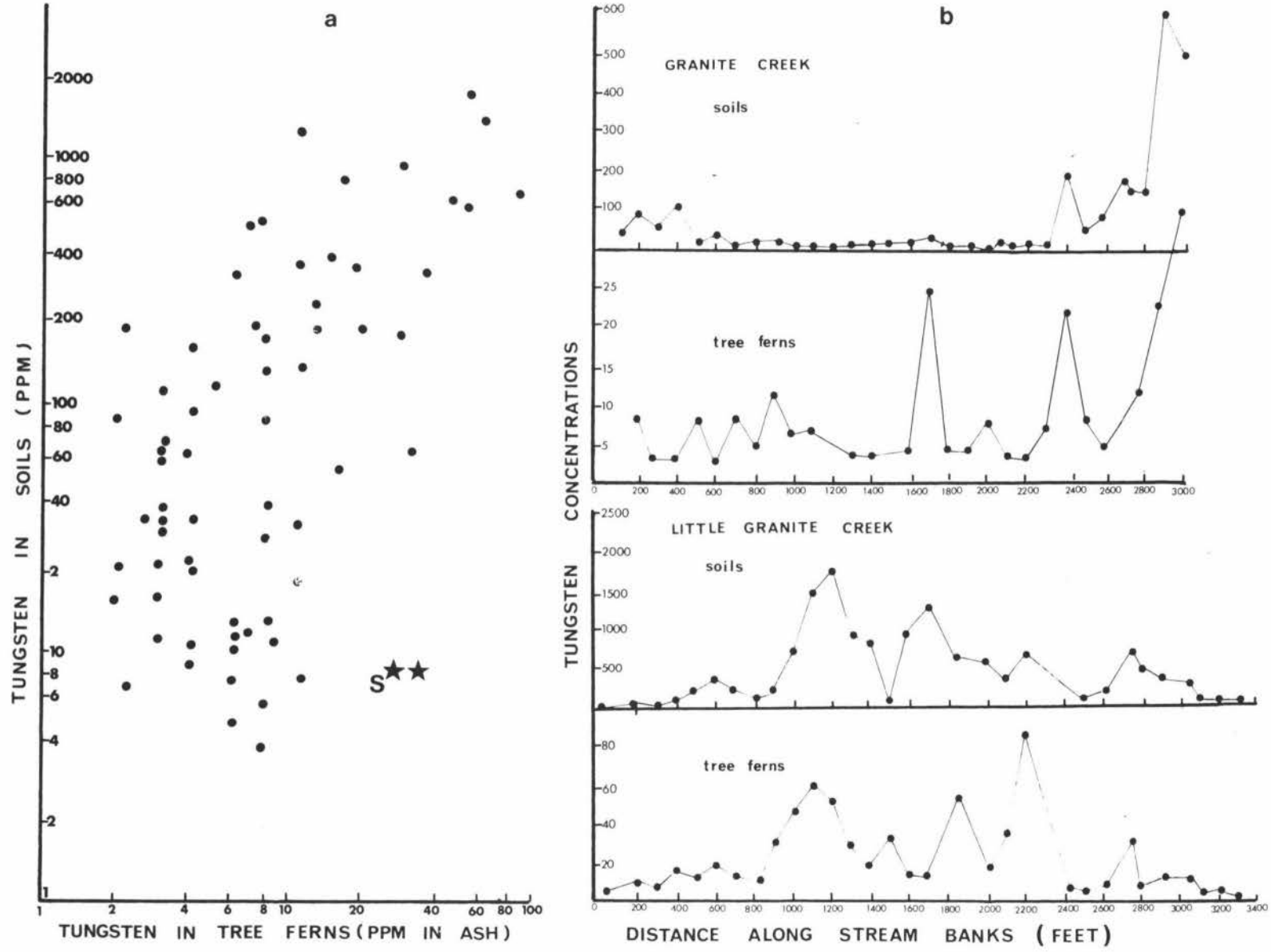


Fig. III.5. Variation of tungsten in stream–bank soils with tungsten in tree–ferns (a) data plot; (b) profiles.

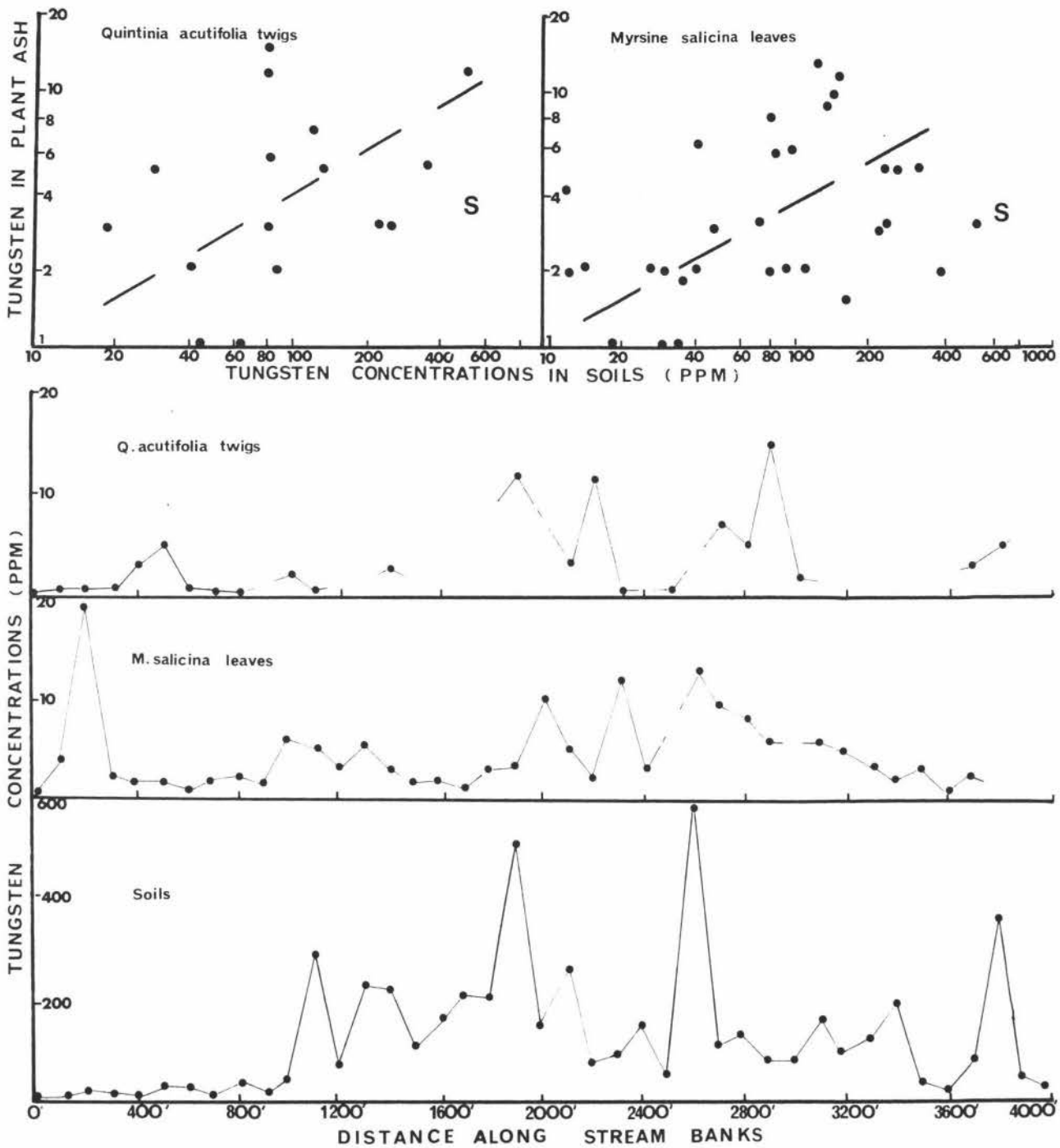


Fig. III.6. Variation of tungsten in ridge soils with tungsten in Quintinia acutifolia twigs and Myrsine salicina leaves (a) data plots; (b) profiles.

same depths as soil samples are taken from (0.2 - 0.6m) Hence provided soil and tree fern samples are taken sufficiently close together, the existence of good correlations are quite possible.

The trees sampled however, particularly the larger kamahi and beech species, have root systems which are far more extensive both laterally and vertically. Their roots therefore sample a large volume of soil in which the tungsten concentration may vary greatly. As a soil sample represents only a small fraction of this volume, poor correlations could result.

Variations in soil properties from one site to another could also have an effect on the correlation, again more so for trees than for ferns because of the difference in soil valumes sampled by their roots.

It is also possible that the presence of ore bodies, which because of ground slope and other factors, may not be manifested in the soil immediately above them but are penetrated by tree roots, may result in high tree values in the absence of high soil values.

(d) Conclusions

In this section the possible usefulness of manganese, lead and tin as pathfinders for tungsten has been demonstrated.

It has also been shown that the tungsten concentration in the leaves of the tree ferns Cyathea medullaris and Dicksonia squarrosa correlated well with its concentration in the soil. However Fig. III.5(a) shows that even the existence of a very highly significant relationship does not permit very reliable prediction of soil concentration from the plant concentration.

Because no new relevant information is gained by analysing the tree ferns it is unlikely that the exploration geochemist would want to stop soil sampling on stream banks and sample only tree ferns. However, the enormously faster nature of fern sampling compared to soil sampling means that, in cases of special urgency, and, for where soil samples were difficult to obtain, tree fern

sampling along stream banks could be used to detect soil anomalies successfully.

The tungsten content of trees, particularly the larger species, did not correlate well with soil tungsten. The possible causes of this were the subject of an investigation described in the next section. These possible causes include variation in (i) tungsten concentration laterally and vertically in the soil, (ii) percentage soluble tungsten in the soil, (iii) tungsten concentration in the trees.

With this type of mineralisation, occurring as it does in narrow veins, one of the biggest problems in exploration is to trace the position of the veins. In areas such as that at Barrytown, faulting, scarcity of outcrops, landsliding, soil creep and leaching all render the tracing of the veins by visual and soil analysis methods very difficult.

For this reason, it was decided to investigate the suitability of plant sampling for tracing tungsten-bearing veins. Because tungsten concentrations were found to be higher in the trunks than in the leaves or twigs of trees (Table III.4), it was decided to restrict sampling to trunks.

The correlation results indicate that the relationships between plant and soil concentrations are equally significant on ash and dry-weight bases. Because the vegetation is ashed before analysis, it is easier to calculate data on an ash-weight basis, and so this procedure was adhered to.

B. FURTHER INVESTIGATIONS

1. Introduction

The aims of these further investigations were twofold. First, it was hoped to determine the cause or causes of the poor tree-soil tungsten correlations, and secondly, to determine whether tree-trunk analysis could be used successfully to locate tungsten-bearing veins.

With regard to the first aim, the results of the pot trials described in Section II of this thesis indicated that, provided that the plants are of similar age and size, and that the physical and chemical properties of the soil are constant, then a good tree-soil relationship could be obtained. The relative importance of these factors would best be determined by carrying out a series of further pot trials in which the factors are varied one at a time, but a shortage of time necessitated the use of field data instead.

The tree ferns sampled covered a wide range of size and age, yet their tungsten concentration still gave a very highly significant correlation with that in the soil (Fig.III.5). This suggests that the absence of a significant tree-soil relationship is due primarily to variation in soil properties, which because of the larger root systems of trees, would have a greater effect on trees than on ferns. The field results presented in this section tend to support this supposition.

The second aim of this section is of more direct value to exploration, but requires a good deal of field work before definite conclusions can be made. Restrictions on the time and money available for this work meant that only a brief investigation of this aspect could be carried out, but the results that were obtained are very promising.

2. Investigation of poor tree-soil correlations

(a) Variation of tungsten with distance into trunk

(i) Sampling

Trunk slices were taken from several trees, including the species *Nothofagus menziesii*, *Weimannia racemosa* and *Quintinia acutifolia*, growing in an area of deep landslide material and soil, which contained an average of 200 ppm tungsten.

(ii) Results and discussion

Table III.8 shows results typical of those found for the three species. The tungsten concentration is generally highest in the outer trunk, often decreasing steadily towards the centre. As the percentage ash decreases towards the centre of the trunk, this trend is not generally true for dry-weight data. The bark generally contains a lower concentration of tungsten than the outer wood on a ash-weight basis, but a higher concentration on a dry-weight basis.

These results indicate that as well as being the easiest to sample, the outer trunk contains more tungsten and is therefore also more suitable for analysis.

The three species also show surprising similarity in their tungsten concentration, particularly in the outer trunk, suggesting that their mode of response to soil tungsten is similar.

It is now necessary to examine the variability in the tungsten concentration of the outer trunk at various points on the circumference, for sampling purposes, and to examine the effect that the age of the tree has on its tungsten concentration.

(b) Variations in concentration of tungsten in trunk and surrounding soil

(i) Description of site

Three *N. truncata* trees growing near Ridge A (Fig. III.0), which was approximately east-west, were chosen for this study. They were of similar diameter (range 24-30 cm) and were found to be of very similar age (70 - 76 years). One

Table III.8

Variation in tungsten concentration with distance into trunk

Species	Age (yrs)	Diam. (cm)	No. of annual rings counted from centre of trunk	Tungsten conc. (ppm in ash)
N. truncata	63	27	0-20	10
			21-30	10
			31-40	18
			41-50	17
			51-63	18
			Bark	6
W. racemosa	57	12	0-20	2
			21-40	4
			41-50	13
			51-57	26
			Bark	7
Q. acutifolia	51	10	0-20	10
			21-40	20
			41-51	25
			Bark	14

of the trees was growing on the crest of the ridge, which was very narrow at this point; the other two were approximately 9m down the sides of the ridge to the north and south respectively. The slope on each side was approx. 35^{o}, and the soil consisted of a dark brown A horizon and a deep B horizon which was lighter in colour and contained many rock fragments.

(ii) Sampling

Trunk slices were cut at approx. 0.5 m above ground level. A further slice at a height of 1.5 m, and root samples, were taken from the centre tree. Four soil samples (both A and B horizons) were taken at distances of 1.5 m from each tree, at bearings of north, south, east and west. After air-drying, the 100 mesh fraction was removed for analysis.

The trunk slices were divided into four corresponding quadrats, and the outer 2.5 cm of each removed for analysis. The bark was also removed and analysed separately.

(iii) Results and discussion

The results of (Table III.9) show that the variability in the lower trunk data, given by the range %, or the range in values as a percentage of the smallest value, lies between that for the A and B horizon soils.

The root concentrations for the centre tree are higher than those in the trunk, and show a greater variability, while the data for the higher trunk are lower, and show a considerably smaller percentage range. This trend of reductions in tungsten concentration and percentage range in going from roots to lower trunk to higher trunk possibly continues through to the branches and then leaves and twigs.

However trunk sampling at chest height (approx 1.5 m) should give a suitable compromise between tungsten concentration and variability, the percentage range at this height being considerably lower than that in the surrounding soil.

This demonstrates that variation of tungsten concentration over small distances in the soil is a factor of more importance in producing poor correlations than is variation in the trunk.

Table III.9

Trunk and soil variability data

Tree 1. North of ridge

	Wood	Bark	A horizon	B horizon
Range	5.6-10.0	6.7-9.4	90-185	80-155
Average	7.4	7.6	137	127

Tree 2. On ridge

	Wood 0.5 m	Bark 0.5 m	Wood 1.5 m	Bark 1.5m	Roots	A horizon	B horizon
Range	6.5-10.4	6.8-12.6	5.8-8.2	6.0-7.7	45-92	85-120	75-135
Average	8.2	9.7	6.9	6.6	70	95	112

Tree 3. South of ridge

	Wood	Bark	A horizon	B horizon
Range	7.2-10.2	7.7-9.2	110-140	90-135
Average	8.3	8.6	125	100

Average range percent

	Roots	Wood	Bark	Wood	Bark	A Horizon	B horizon
Height(m)	0.5-1.0	0.5	0.5	1.5	1.5	0.25	0.5
Range %	104	61	47	27	29	47	87

(c) Effect of tree age on concentration of tungsten in outer trunk

(i) Sampling

Slices were taken from groups of trees growing close to one another at a number of sites, to examine the effect of tree age and size on the tungsten concentration in the outer trunk. In order to average out variations, a complete ring was cut out, ashed and mixed before removing a portion for analysis.

(ii) Results and discussion

The results (Table III.10) demonstrate that there is as much variation in the tungsten concentration in trees of the same species, age and size as there is between different species of trees of different age and size.

For example, the tungsten concentration in the three similar N. truncata specimens from Site 1 and the two similar specimens at Site 2, show a greater range than do the Site 3 trees, which are all different species and cover a far wider range of age and size.

Similarly, at Site 4, the tungsten concentration in the single M. racemosa specimen lies between that in the two N. truncata trees.

These results, with those of part (b), serve to show that differences in the size and age, and even the species of tree, are of less significance in controlling the concentration of tungsten in the trunk than is the natural variation in the properties of the substrate into which their roots penetrate.

Although this does not bode well for using tree trunk analysis to indicate soil tungsten concentrations, it does not preclude the possibility of their use in locating ore bodies.

Several workers have listed the factors which influence the metal concentration of trees (Carlisle and Clevelend, 1958; Warren, Delavault and Fortescue, 1955), but only a few have attempted to determine the relative importance of these factors (Timperley, Brooks and Petersen, 1972),

Table III.10

Variation of tungsten concentration in trunk with species, age and size of tree

Site no.	No. and type of species	Age range (yrs)	Diam. range	Trunk tungsten range (ppm in ash)
1	3 N.t.	70-76	24-30	7.4 - 8.3
2	2 N.t.	63	20-27	4.6 - 7.2
3	1 P.f., 1 N.f., 1 N.m.	75-220	27-46	5.4 - 5.9
4	2 N.t. 1 W.r.	52-53 50	22-23	180-460 190

N.t. Nothofagus truncata
N.m. N. menziesii
N.f. N. fusca
P.f. Podocarpus ferrugineus
W.r. Weimannia racemosa

and certainly no one has attempted to do this for tungsten.

An attempt was made therefore to determine which soil property or properties had the greatest influence on the uptake of tungsten by trees.

(d) Differences in soil properties between sites

(i) Introduction

Two sites nearly 1000 m apart on Ridge A (Fig.III.0) were chosen for this study, the first (Site I) being that used in part (b) (page 87), the same trunk and soil samples being used in each case. A second set of three trees at the second site (Site II) were treated in the same way.

When the trunk and soil (-100 mesh) samples were analysed and averaged, it was found that although Site I had the lowest soil concentration of tungsten, it had the highest concentration of this element in the tree trunks (Table III.11) This is the very type of result that has caused the poor tree-soil correlations, and in this case, because each result is the average of 12 analyses, the differences cannot be due to random sampling variation.

To investigate further the composition of the soils, the 24 soils from each site (12 A horizon and 12 B horizon) were dry-sieved into 10-40, 40-70, 70-100, 100-200 and -200 mesh fractions. The -10 mesh fraction was discarded, and composite B and B horizon samples for the other mesh fractions for the two sites were made by mixing 0.5g from each sub-sample. The results of the investigation of these mesh fractions are tabulated in Table III.12, and are discussed below.

(ii) Tungsten concentration in the various size fractions

The tungsten concentration was found to increase with decrease in mesh size for both the A and B horizons at each site. Also, each mesh fraction at Site II has a higher tungsten concentration than the corresponding mesh size from Site I.

Table III.11

Tungsten data for trunks and soils (-100 mesh) from Sites I and II

Site	Ave. trunk conc. (ppm W in ash)	Average soil concentration (ppm W) A horizon	B horizon
I	8.0	119	113
II	5.7	152	193

Table III.12

Soil size fraction data for Sites I + II

Site and horizon	Mesh fraction	Total ppm W	% by weight	µg W in 100g soil	ppm H_2O soluble W	% H_2O soluble W	soil pH	% organic matter
	10-40	27	67.4	1820	1.3	4.7	4.4	5.5
Site I	40-70	43	22.9	986	1.3	3.1	4.4	11.0
A	70-100	60	3.1	185	1.2	2.0	4.6	11.5
horizon	100-200	95	3.0	289	0.7	0.8	4.4	13.5
	-200	119	2.9	339	0.4	0.3	4.6	10.0
	10-40	25	65.2	1629	2.6	10.2	4.9	4.5
Site I	40-70	45	25.3	1138	2.1	4.6	4.9	8.0
B	70-100	82	3.3	272	1.2	1.4	4.8	9.0
horizon	100-200	102	3.2	330	0.8	0.8	4.8	10.5
	-200	115	3.0	346	0.2	0.2	4.8	18.0
	10-40	40	72.7	2908	0.4	0.9	4.3	14.0
Site II	40-70	75	18.4	1383	0.6	0.8	4.2	18.0
A	70-100	80	2.8	227	1.4	1.7	4.1	17.0
horizon	100-200	136	3.3	453	0.5	0.3	4.1	17.5
	-200	157	2.7	404	0.1	0.1	4.1	15.0
	10-40	40	74.0	2960	0.6	1.5	4.5	7.0
Site II	40-70	125	18.0	2247	0.5	0.4	4.0	12.5
B	70-100	166	2.8	463	1.0	0.6	4.3	14.0
horizon	100-200	191	3.0	563	0.6	0.3	4.3	14.0
	-200	193	2.3	444	0.1	0.1	4.0	13.0

(iii) Amount of tungsten in the various size fractions

To ensure that the actual amount of tungsten present, as well as the concentration, was highest in the Site II soils, the actual amounts present in each mesh size were calculated by weighing every mesh fraction of every subsample. The results (Table III.12) show that the percentage by weight of the different mesh sizes are similar for both sites. Hence when the amounts of tungsten present are calculated (as μg tungsten in 100 g of -10 mesh soil, Table III.12) the tungsten content of the Site II soil is indeed higher than that at Site I.

(iv) Water-soluble tungsten in the various size fractions

To obtain some idea of what proportion of the total tungsten present was available to the plants, the amount of water-soluble tungsten in the various mesh fractions was determined. While there is no guarantee that this accurately reflects the "available" tungsten, it is probably a better guide than that determined by using buffers or dilute acids as these, because they control the pH of the sample solution, can give false results for an element such as tungsten, the solubility of which may be pH-dependent.

The results (Table III.12) show that, although Site II has the highest total tungsten, it has a lower water-soluble tungsten, and this is probably responsible for the lower concentrations of tungsten in the trees.

The course fractions are seen to contain more water-soluble tungsten than the fine fractions. However this is probably a result of dry-sieving, as the coarse particles were seen under the microscope to be coated with smaller particles. These small particles are bound to the larger particles with hydrous oxides of iron and aluminium, the products of weathering of the granitic parent rock. This presents an explanation of the high water-soluble content of the coarse fractions, because at a pH of less than 5, these hydrous oxides can become positively charged, and as a

result tungstate anions, liberated by the weathering of scheelite and wolframite, can bind to them. As this tungsten would be more soluble than are the primary minerals, this could explain the higher water-soluble content of the coarse fractions. Because of this, plant concentrations might be expected to correlate better with the coarse fractions than with the fine fractions of dry-sieved soils. However the greater variation in the tungsten concentration in the coarse fractions prevents this from being the case.

More evidence to support the tungstate binding is presented in part (g).

(v) pH of the various size fractions

The results (Table III.12) show that the pH values are all low. This is partly due to the granitic parent rock which, owing to the chemical nature of the minerals and their products of decomposition, produces an acid soil poor in nutrients, and partly due to the predominance of beech species, which produce a particularly acidic humus (Miller, 1963).

A closer inspection of the results reveals that the Site II samples have a lower pH than the corresponding mesh fractions from Site I, by an average of 0.3 for the A horizon and 0.6 for the B horizon. This lower pH is apparently responsible for the lower percentage water-soluble tungsten at Site II.

(vi) Organic content of the various mesh fractions was determined by loss of weight after heating at 500°C. The results (Table III.12) show that the soil at Site II has a considerably higher organic content than that at Site I, particularly in the coarser fractions, which make up the bulk of the soil. The higher organic content at Site II is probably a result of the greater average age and size of the trees in this area (the area around Site I hay have been burnt off about 80 years ago),

and the lower pH could result from this.

The inorganic properties of the soil are less likely to have caused the lower pH at Site II, because the parent rock, being similar at both sites, would produce similar types and quantities of products such as clays on weathering.

(e) Water-soluble tungsten and pH

To examine further the association between water-soluble tungsten and pH, many more soil samples were tested. It was found that, because of the differences in the physical and chemical composition of individual samples, an association between the two factors was obvious only when the results for many soils from one area were averaged and compared with those from another, as was the case for Sites I and II.

The ridge soils (-100 mesh) were found to have a lower average pH and percentage water-soluble tungsten (4.9 and 0.79 respectively) than those from the creek banks (5.3 and 0.85 respectively). The lower pH of the ridge soils is probably associated with the greater leaching they have undergone.

(f) The effect of distance from source on the distribution of tungsten between coarse and fine soil fractions

The success of a plant-soil correlation will depend, amongst other things, on the soil mesh fraction chosen for analysis containing a constant proportion of the total present in the soil. An investigation was carried out therefore to determine if this was the case.

Sites were chosen on each of the creek banks where tungsten-bearing veins outcropped, and a third site on Ridge A where the soil was tungsten-rich and contained many quartz fragments was selected. A series of 10 soil samples were taken at 100' intervals down from each of these sites. After

drying, the (a) 10-40 and (b) -100 fractions were removed by dry-sieving and analysed for tungsten. The ratios for (a)/(b) were plotted for each series (Fig.III.7). They show a striking similarity in their pattern, particularly for the two creek-bank series, which reach a minimum at approximately 600'.

The initial downward curve could be caused by the physical weathering of the scheelite particles as they are moved further from the source. A possible explanation for the subsequent rise in the ratio is as follows.

As the soils were dry-sieved, the coarse particles are coated with smaller particles bonded to them with hydrous oxides of iron and aluminium. At low pH these oxides become positively charged, and tungstate anions released by weathering of the minerals can bind to them, for example according to the reaction:

$$2Fe(OH)^{+} + WO_4^{2-} \rightleftharpoons (FeOH)_2WO_4$$

As pointed out on pg 97 , this binding would explain the higher percentage water-soluble tungsten in the coarse fractions.

(c) Distribution of tungsten between magnetic and non-magnetic soil fractions

A magnetic separation of a composite soil sample was carried out using a Frantz Isodynamic magnetic separator (Model L-1). The 60-80 mesh fraction was found to be the most suitable for soils, and, better separation was achieved by keeping the current and forward slope constant and altering only the side slope.

The initial separation was carried out at a side slope of 25°. Portions of the two fractions were removed for analysis, then the less magnetic fraction was separated again, this time at a side slope of 15°, and so on through side slopes of 12.5°, 10°, 7.5° and 5.0°. After each separation portions of both fractions were removed for analysis, the remainder of the more magnetic fraction discarded, and the remainder of the less magnetic fraction reseparated at the

at the next lower side-slope. Below 5° the vibration of the instrument prevented any further differentiation of the less magnetic fraction.

The results (Table III.13) clearly indicate that the more magnetic the fraction, the higher its tungsten concentration, and overall, the magnetic fraction (that capable of separation at a side slope of 5° or greater) comprised 8.4% of the total sample weight, yet contained 20.5% of the total tungsten. As the tungsten mineralisation is made up of 98 - 99% non-magnetic (Flinter, 1959) scheelite and only 1-2% magnetic wolframite (J.A.C. Painter, personal communication) this 20.5% is far in excess of that due to the wolframite present. This strongly supports therefore the hypothesis that much of the tungstate released by weathering is bound to the hydrous iron oxide material.

(h) Variation in percentage water-soluble tungsten with distance from source

Water-soluble tungsten determinations were made on the same soils used in part (f) (pg 99). Although no definite pattern emerged, it was evident that soils in the vicinity of outcrops had a lower percentage water-soluble tungsten (approximately 0.1 - 0.3%) than those further away. This might be expected to result in plant anomalies smaller than those shown by the soil, and, as shown in Fig. III.5, this is often the case.

(i) Discussion and conclusions

The results of these investigations have demonstrated that tree size and age, and even the type of species (at least among those investigated) are relatively unimportant factors in causing poor tree-soil correlations.

The percentage of water-soluble tungsten was found to vary between sampling sites, and the pH of the soil was implicated as being partly responsible for this, the pH in turn being influenced by the organic content of the soil.

Distance from the source of the tungsten was also

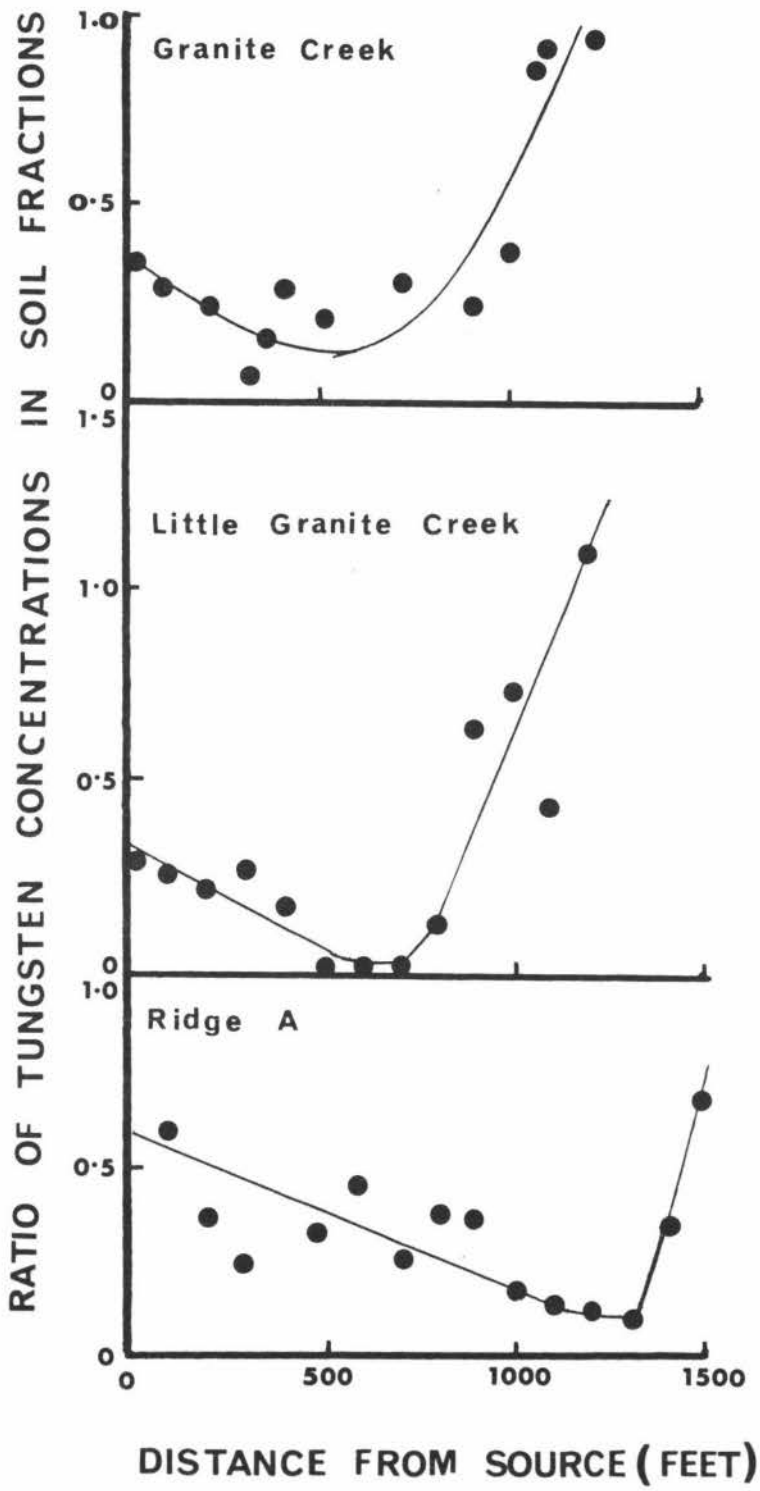


Fig. III.7. Distribution of tungsten between 10–40 and –100 mesh fractions as a function of distance from source.

Table III.13

Data for magnetic separation[a] of soil (60-80 mesh)

Side slope (degrees)	Tungsten concentration (ppm)	
	More magnetic fraction	Less magnetic fraction
25	1940	215
15	1215	215
12.5	545	200
10	325	185
7.5	230	140
5	210	125

[a] Current: 1.0 Amp. Forward slope: 20°

considered to have an effect on the water-soluble tungsten, due to the effects of physical and chemical weathering.

When put to the test, it was found that already significant correlations, such as those for the tree-ferns, were slightly improved by plotting water-soluble instead of total tungsten (Fig. III.8). However the poor tree-soil correlations were not improved; indicating that the level of water-soluble tungsten in the soil can vary greatly over small distances such as those encompassed by a tree's roots.

Because (1) the total tungsten can vary markedly over small distances, and (2) even where it does not, the percentage water-soluble tungsten does, it must be concluded that the tungsten concentration in the trunks of tree species with extensive root systems cannot be successfully used to determine the concentration of tungsten in one soil sample relative to that in another.

The failure of biogeochemical exploration in this application however does not, as is demonstrated in the next section, preclude its use in the detection of tungsten-bearing veins.

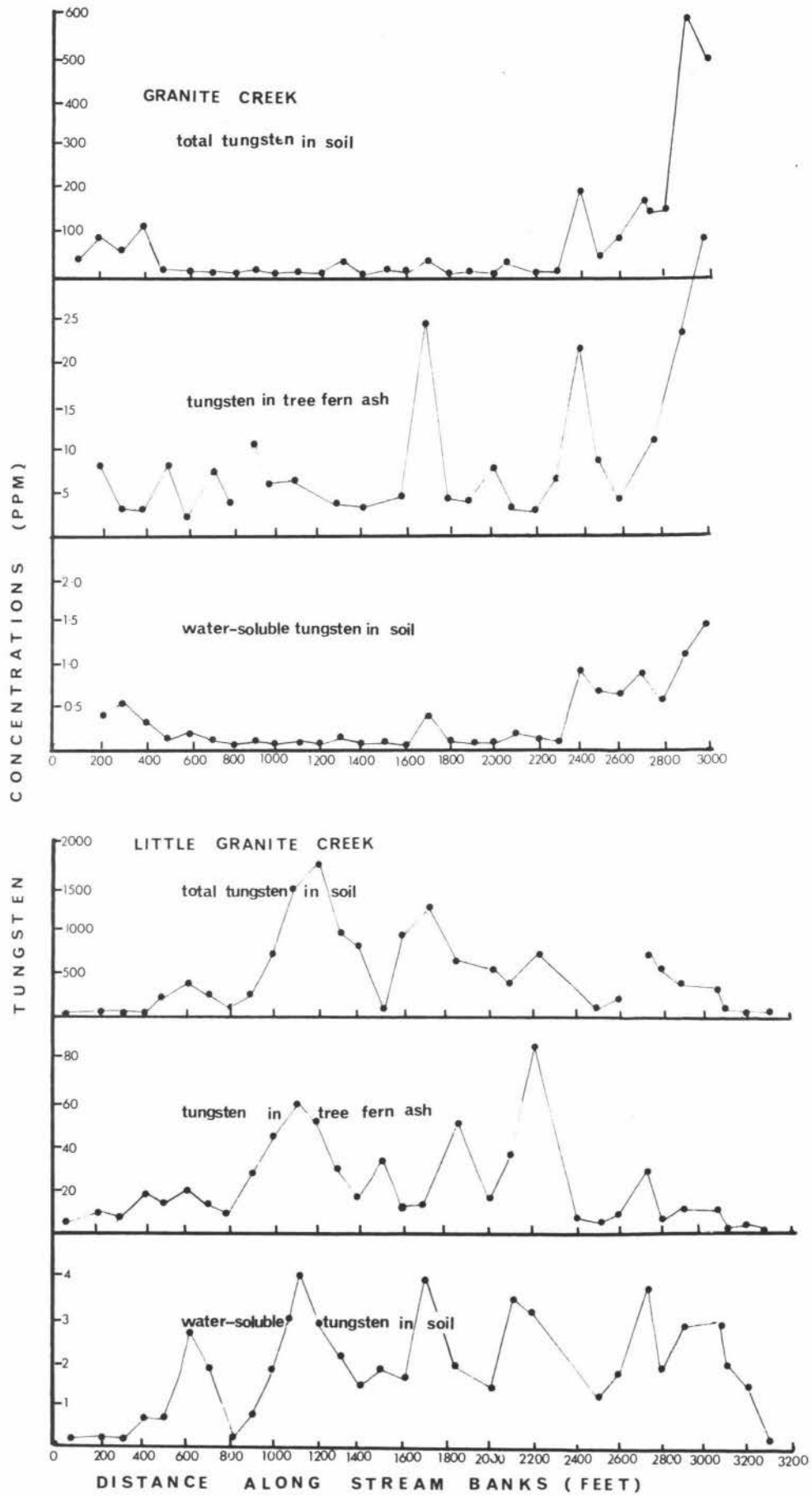


Fig. III.8. Variation of total and water–soluble tungsten in stream–bank soils with tungsten in tree ferns.

3. The use of trunk sampling in locating tungsten-bearing veins.

(a) Introduction

The results of the preceding investigations have shown that the tungsten concentration of trees is not an accurate guide to that in the soil. However the roots of a tree growing in soil overlying tungsten-bearing veins may extend into the veins, and this being the case, the roots will be in an environment of enormously higher tungsten than the roots of trees even a few feet away. Hence, despite the fact that the water-soluble tungsten is variable and is generally lower nearer the veins (pg 101), the tree will almost certainly contain a significantly higher concentration of tungsten than its neighbours whose roots penetrate the vein to a lesser extent or not at all.

An investigation was carried out therefore to determine whether the position of tungsten-bearing veins could be located by trunk analysis, and to determine whether high trunk concentrations caused by the presence of veins could be distinguished from those resulting merely from high concentrations of transported tungsten in the soil.

(b) Description of areas

Two contrasting areas were chosen for investigation.

(i) Area containing transported tungsten

In this area, the bedrock lay under a considerable depth (in excess of 12') of landslide debris and transported soil. The ground slope was 40°, bearing east-west. A trench had been dug by Carpentaria staff and at its deepest point (12') had still not reached bedrock. Many small tree roots, which are responsible for most of the nutrient uptake, were observed in the trench down to this depth. Only isolated quartz boulders were observed in the trench, and the consistent pattern of vertical distribution of the tungsten in the soil indicated that the tungsten had been transported from a source some distance uphill.

(ii) Area containing tungsten-bearing veins

In this area, outcrops of tungsten-bearing veins were present, and trees were found growing close to these outcrops in as little as 0.5m of soil, with many of their small roots dispersed throughout the veins. The veins, as did those observed in other outcrops in the Barrytown area, had an approximately north-south strike.

(iii) Sampling

Trunk, root and soil samples were collected from the region of the trench in area (i) and from near the outcrops in area (ii). The trunk samples were taken from the east and west sides of the trees at area (ii) and from the up-and-down slope sides of the trees at area (i). The soil samples were taken near the tree roots at depths of 0.3 - 1 m. Tree root samples were washed carefully to remove soil contamination.

(c) Results and discussion

(i) Trunk concentrations

The results (Table III.14) show that the presence of tungsten-bearing veins does result in very high concentrations of tungsten in the tree trunks.

An outstanding feature of these results is that whereas at area (i) the tungsten concentration in the upslope side of the trunks (that nearest the source of tungsten) is only very slightly higher than that in the downslope side, the tungsten concentration in the trees near the outcrops (area (ii)) are markedly higher in the side adjacent to the veins than in the opposite side.

This uneven distribution of tungsten in the trunks must result from the roots feeding the side of trunk nearest the veins being in an environment of higher tungsten, and is of great significance for biogeochemical prospecting, as it provides a means of determining whether the high trunk values are due to the presence of veins or merely to soil tungsten transported from elsewhere.

Although some earlier workers have pointed out the

importance of sampling at different points on the tree to obtain a representative sample (Brooks, 1972; Warren, Delavault and Fortescue, 1955), to the author's knowledge, the possibility of utilising this effect in mineral exploration has not previously been reported.

(ii) Distribution of tungsten in trunk

In view of the high concentrations of tungsten in some of the trees growing near the veins, it was decided to investigate the distribution of tungsten with depth into the trunk of these trees with those from areas of transported tungsten (Table III.8). Slices from two N. truncata specimens were taken. The results (Table III.15) show an initial decrease from the outside towards the centre followed by a marked increase. This trend, which follows the same pattern for ash and dry weight based data, differs markedly from that for the examples in Table III.8, and suggests that trees growing in high-tungsten environments may be capable of storing excess tungsten in their older dormant wood.

(iii) Soil versus trunk analyses

Unlike trunk analysis, the analysis of soils from the two areas would not distinguish between the two areas in the absence of outcrops, as the higher range of soil values at area (ii) was caused mainly by the physical weathering of the outcrops, which resulted in scheelite particles dropping on to the soil below.

(d) Transect across veins

(i) Introduction

When the soil cover is greater than the 0.5 m found at area (ii), fewer tree roots will penetrate the veins and the tree concentration might be expected to be lower as a result. To determine whether the veins could be located under deeper soil, a site was chosen which lay between two outcrops of tungsten-bearing veins but which was covered in a deep layer of soil. A trunk-sampling transect was carried out across this site in a direction (east-west)

Table III.14

Comparison of tree and soil tungsten data for areas of (i) transported tungsten, and (ii) tungsten-bearing quartz veins

Area	No. of samples	No. of species	Ave. trunk W concn.	Ave. root W concn.	Ave. soil W. concn.	Range in soil W concn.
(i)	7	3	39 (upslope side) 36 (downslope side)	495	340	230-530
(ii)	5	3	300 (side adj. to veins) 140 (side opp. to veins)	1150	1250	290-3100

Table III.15

Distribution of tungsten in trunks of two trees growing over tungsten-bearing veins

No. of annual rings counted from centre of trunk	Ave. tungsten concentration (ppm)			
	(1)		(2)	
	ash wt.	dry wt.	ash wt.	dry wt.
0-10	940	4.5	40	0.26
11-20	560	1.4	29	0.15
21-30	390	1.0	25	0.13
31-40	115	0.3	45	0.23
41-53	375	1.7	63	0.36
Bark	150	5.1	42	1.3

perpendicular to the strike of the veins, and the samples were analysed to determine if a peak of high values was found above the calculated position of the veins.

Because the veins are so narrow (General Introduction) it was considered necessary to sample at as small intervals as possible, certainly at least as small as the 5-10 m suggested by Kovalevsky (1966). Because of this, it was not possible to restrict sampling to only one or two species as suggested by some workers (Carlisle and Cleveland, 1958). In any case, the results of the trunk variability study (Table III.9) suggest that the different species respond in a similar fashion to tungsten in the substrate.

(ii) Sampling and analysis

The transect was commenced at approx. 20 m above the veins and continued to approx. 40 m below the veins. The slope of the transect was 35° and the bearing approximately east-west. The width of the transect was restricted to approx. 4 m and all the trees within this belt with a diameter greater than 7 cm were sampled. In order to reduce sampling and analysis time, only one sample was taken from each tree, being taken from the downslope side of the trees above the veins and from the upslope side of those below the veins.

In the laboratory, the bark was removed from the outer trunk and both were analysed separately.

(iii) Results and discussion

The results of the transect are shown diagrammatically in Fig. III.9. Data for individual trees are given in Appendix 2.

The wood analyses show a peak of high values very near the veins; it may be concluded that the position of the veins could have been located by trunk analysis, at least within $\pm$ 3 m, and possibly more accurately if more trees had been sampled, and/or if double sampling of each tree had been carried out.

The necessity for many trees to be sampled is also

shown by the fact that some trees near the veins contained only low concentrations of tungsten, probably due mainly to shallow root systems; it is those trees with deeper roots that one must be sure of sampling, and this can only be ensured by collecting large numbers of samples. For example, if only 20 trees instead of 40 had been sampled in this transect the veins could easily have been missed.

The higher value at the top of the transect suggests the presence of more (non-outcropping) veins.

The results of the bark analyses did not indicate the position of the veins, and henceforth only trunk wood will be sampled.

(e) Conclusions

The feasibility of using multiple-species trunk-sampling to locate tungsten bearing veins under soil and to distinguish this from transported soil tungsten has been demonstrated.

The reliability of the method must now be tested by carrying out further transects over known tungsten-bearing veins, and in known unmineralised areas. Only then will the method be ready for routine application in unknown areas.

This method of locating veins is enormously faster than soil sampling, particularly in areas such as Barrytown, where rugged topography and the presence of layers of tree litter and roots render soil sampling very slow, and for relatively little extra expenditure could yield valuable information additional to that provided by other methods.

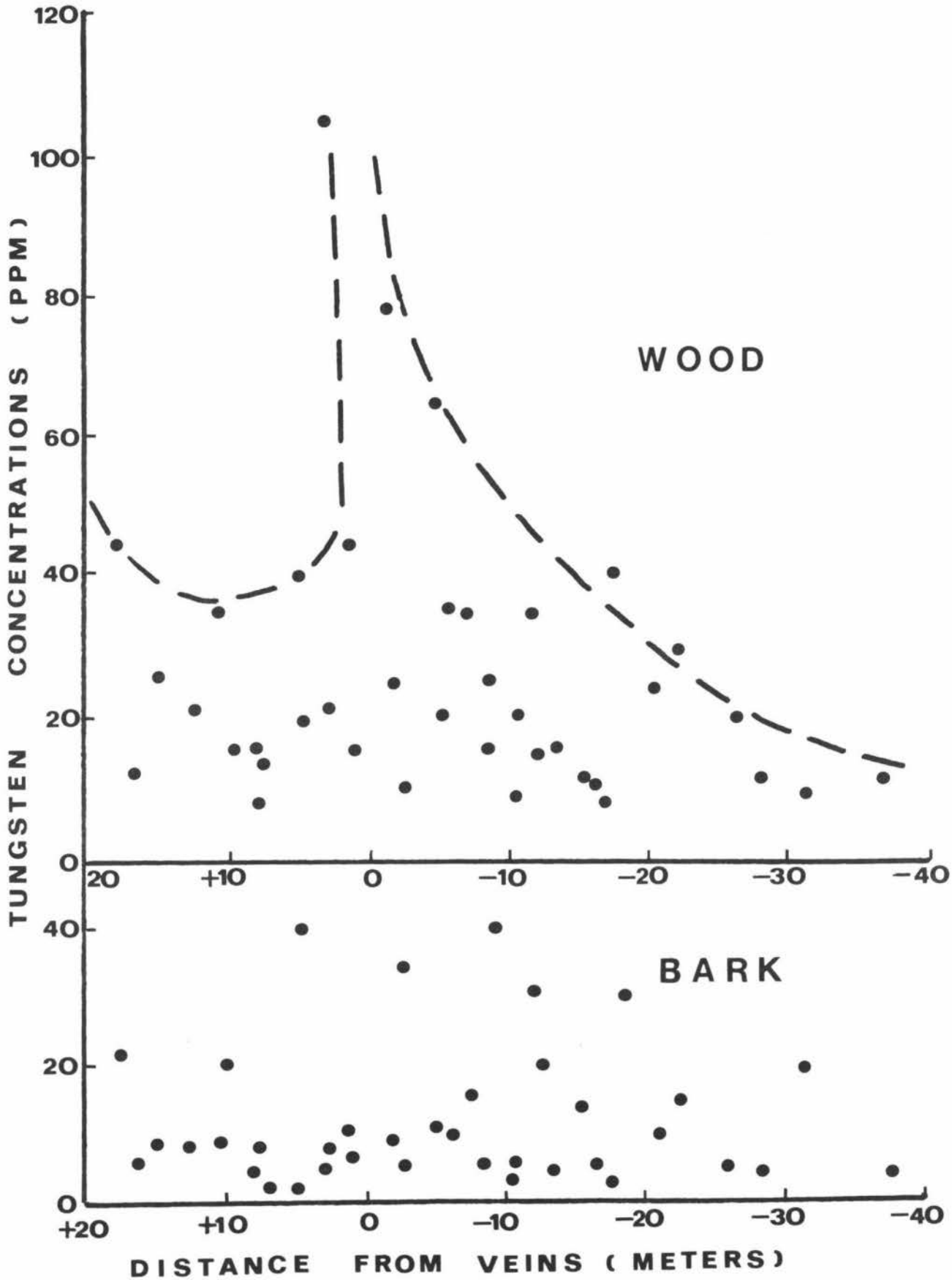


Fig. III.9. Transect across tungsten–bearing veins.

SUMMARY

AND

GENERAL

CONCLUSIONS

The aims of this thesis, as mentioned in the General Introduction, were threefold:

1. To develop rapid, sensitive and reproducible procedures for the determination of tungsten in vegetation, soils and rocks, in any concentration, on a routine basis.

2. To determine whether biogeochemical prospecting has any useful role to play in the detection and pin-pointing of tungsten ore bodies, and to compare its success with that of soil sampling, particularly in areas subject to leaching, soil creep and landsliding.

3. To investigate some of the factors which obscure the plant-substrate relationship with respect to tungsten, to assist in the interpretation of future field work.

The results presented in Sections I, II and III of this thesis show that the above aims have largely been achieved.

The analytical section (Section I) showed that, by careful selection of conditions, a large quartz-optics emission spectrograph could be successfully used to analyse low concentrations of tungsten in soils and rocks, but was not suitable for the analysis of vegetation.

The colorimetric procedure developed allowed for the detection of tungsten in vegetation, soils and rocks at concentrations down to 0.1 ppm with extremely high productivity.

The results of the tungsten uptake experiment (Section II) showed that the use of plant analysis to gain information on the concentration of tungsten in the soil was at least feasible. However field results (Section III) showed that while this plant-soil relationship held for species with small root systems such as tree ferns, variability in soil properties such as pH, rather than variability in the size, age and even species of tree, prevented this being the

case for tree species.

Nevertheless it was found that trunk analysis could be successfully used to locate tungsten-bearing veins, and that the presence of these could be distinguished from transported soil tungsten.

The specific findings and achievements of this project were:

(i) The development of an emission spectrograph procedure for the analysis of tungsten in soils and rocks down to 10 ppm;

(ii) The development of a colorimetric procedure for the analysis of vegetation, soils and rocks with a sensitivity of 0.1 ppm and very high productivity;

(iii) The demonstration that the concentration of tungsten in the various organs of young plants of Nothofagus menziesii are closely related to the tungsten concentration in the soil, although the great majority of this tungsten, when taken up over a short period at least, is concentrated in the roots,

(iv) The demonstration of the possible usefulness of manganese, lead and tin as pathfinders for tungsten;

(v) The demonstration that tree fern sampling may be successfully used to detect tungsten anomalies in the soil;

(vi) The demonstration that poor tree-soil correlations are caused largely by the variation in percentage water-soluble tungsten in the soil, resulting from variation in pH and other factors;

(vii) The demonstration that trunk sampling can be successfully used to locate tungsten-bearing quartz veins, without restriction of the number and type of species.

I consider that future studies in the areas of tungsten mineralisation should be carried out with the following aims:

(1) To substantiate further the validity of using manganese, lead and tin, and arsenic, as pathfinders for tungsten.

(2) To test the reliability of trunk sampling in the locating of tungsten-bearing veins, and to determine through what depth of soil and debris this can be done.

(3) To compare the success of this method of locating veins in areas of different geological, climatic and topographical environments, to determine whether the method is of general application.

Appendix 1

Fresh, dry and ash weights for pot trial plants

Plant	Organ	WEIGHTS (g)			PERCENTAGES		
		Fresh	Dry	Ash	Dry/fresh	Ash/fresh	Ash/dry
	L	2.42	0.63	0.12	26.1	4.9	19.1
1	S	6.69	2.98	0.21	44.7	3.1	7.2
	R	28.1	6.9	0.91	24.7	3.2	15.3
	L	6.61	3.15	0.23	47.6	3.5	7.3
2	S	11.98	6.07	0.34	50.1	2.8	5.6
	R	57.4	15.3	1.86	26.6	3.2	12.1
	L	6.87	4.07	0.19	59.0	2.8	4.7
3	S	5.95	2.79	0.14	47.0	2.4	5.0
	R	34.7	9.0	1.25	26.0	3.3	13.9
	L	3.66	1.80	0.12	49.2	3.3	6.7
4	S	9.04	4.05	0.23	44.8	2.5	5.7
	R	25.8	7.4	0.50	28.6	1.9	6.7
	L	6.79	3.37	0.18	49.6	2.6	5.3
5	S	10.32	4.93	0.23	47.7	2.2	4.7
	R	46.1	13.5	1.50	29.1	3.2	11.1
	L	4.37	2.10	0.14	48.1	3.2	6.7
6	S	7.84	3.91	0.19	49.8	2.4	4.9
	R	28.8	7.2	0.80	25.8	2.9	11.0
	L	5.88	2.48	0.18	42.3	3.1	7.2
7	S	8.89	4.09	0.21	46.0	2.4	5.2
	R	17.2	7.1	0.68	41.2	3.9	9.6
	L	8.67	9.00	0.28	46.2	3.2	7.0
8	S	22.98	10.72	0.57	46.8	2.5	5.3
	R	51.0	16.2	2.75	31.8	5.4	16.9
	L	4.61	1.95	0.11	42.5	2.4	5.7
9	S	17.92	8.13	0.56	45.2	3.1	6.9
	R	24.5	7.7	1.10	31.4	4.5	11.0
	L	7.51	3.38	0.25	45.2	3.3	7.4
10	S	11.08	5.02	0.27	45.4	2.8	5.4
	R	30.0	12.0	1.20	40.2	4.0	10.0
	L	5.82	2.74	0.18	47.2	3.1	6.6
11	S	10.32	5.00	0.31	48.5	3.0	6.2
	R	40.7	12.6	1.51	31.0	3.7	12.0
	L	6.77	3.01	0.25	44.3	3.7	8.3
12	S	9.12	4.25	0.25	46.5	2.7	5.9
	R	40.3	13.0	1.89	32.5	4.7	14.6
	L	5.97	2.65	0.24	44.3	4.0	9.1
13	S	14.22	6.87	0.43	49.3	3.1	6.2
	R	36.0	10.6	1.22	29.6	3.1	11.5

L : leaves S : stems R : roots

Appendix 2

Individual plant data for trunk-sampling transect

Tree no.	Distance from veins (m)	Species	Trunk diam (cm)	W conc n. (ppm in ash) wood	bark
1	18	Weimannia racemosa	45	45	20
2	16.5	W. racemosa	23	12	6
3	15	W. racemosa	23	25	9
4	12.5	Quintinia acutifolia	7	20	8
5	10.5	Metrosideros lucida	40	15	9
6	10	Myrsine australis	8	15	20
7	8	W. racemosa	20	8	5
8	8	W. racemosa	7	15	7
9	8	A. acutifolia	10	12	4
10	7.5	M. australis	13	15	3
11	5	N. truncata	15	20	3
12	5	Q. acutifolia	7	40	40
13	3	Q. acutifolia	12	20	8
14	3	Q. acutifolia	15	105	6
15	1.5	Q. acutifolia	10	45	10
16	1	Q. acutifolia	10	15	6
17	-2	M. australis	7	25	9
18	-2	Q. acutifolia	15	77	35
19	-2.5	Q. acutifolia	15	10	6
20	-5	N. truncata	38	20	12
21	-5	M. lucida	20	65	-
22	-6	Q. acutifolia	13	35	10
23	-7	W. racemosa	13	35	15
24	-8.5	Q. acutifolia	10	15	6
25	-8.5	W. racemosa	13	25	40
26	-10.5	N. truncata	15	9	6
27	-10.5	W. racemosa	15	20	5
28	-11.5	Q. acutifolia	15	35	30
29	-12	Q. acutifolia	28	15	20
30	-13	W. racemosa	20	15	5
31	-15	Q. acutifolia	8	12	15
32	-16	Q. acutifolia	8	11	5
33	-17	N. truncata	30	9	3
34	-18	Q. acutifolia	10	45	30
35	-20.5	W. racemosa	40	.25	10
36	-22	Q. acutifolia	13	30	15
37	-26	N. truncata	13	20	6
38	-28	N. truncata	30	11	6
39	-31	M. australis	30	9	20
40	-37	N. truncata	35	12	5

INDEX OF AUTHORS

REFERENCES

Ahrens, L.H. (1943), J.S. Afr. Chem. Inst. 23 21-26, Spectrochemical determination of wolfram in siliceous material.

Ahrens, L.H. (1954), Geochim. Cosmochim. Acta 5 49-73, The lognormal distribution of the elements.

Ahrens, L.H., and Taylor, S.R. (1961), Spectrochemical Analysis. Addison - Wesley, Reading.

Allen, S.H., and Hamilton, M.B. (1952), Analytica Chim. Acta 7 483-493, The estimation of molybdenum and of tungsten by dithiol.

Aull, J.C., and Kinard, F.W. (1940), J. Biol. Chem. 135 119-121, The determination of tungsten in biological materials.

Bagshawe, B., and Truman, R.J. (1947), Analyst 72 189-193, A method for the determination of tungsten in steel, using toluene -3,4- dithiol. The removal of molybdenum interference by selective extractions.

Baylis, G.T.S., McNabb, R.F.R., and Morrison, T.M. (1963), Trans. Brit. Mycol. Soc. 46 378-384, The mycorrhizal nodules of Podocarps.

Bickford, C.F., Jones, W.S., and Keene, J.S. (1948), J. Am. Pharm. Assoc. Sci. Ed. 37 255-261, Microdetermination of molybdenum and tungsten in organic materials.

Boswell, C.R., and Brooks, R.R. (1965), Appl. Spectr. 19 147-150, Improved methods for the measurement of spectral line intensities.

Bowden, P. (1964), Analyst 89 771-774, A geochemical field method for determining tungsten in soils and stream sediments.

Bowen, F.E. (1964), Sheet 15, Buller, Geological map of New Zealand 1 : 250,000. D.S.I.R., Wellington, New Zealand.

Bowen, H.J.M. (1960), Biochem. J. 77 79-82, The determination of tungsten in biological material by activation analysis.

Brookes, C.J., Betteley, I.G., and Loxston, C.M. (1966), Mathematics and statistics for chemists, Wiley, N.Y.

Brooks, R.R. (1972), Geobotany and biogeochemistry in mineral exploration, Harper and Rowe, N.Y.

Brooks, R.R., and Lyon, G.L. (1966), N.Z. Jl. Sci. 9 706-718, Biogeochemical prospecting for molybdenum in New Zealand.

Brundin, N. (1939), U.S. Pat. 2158980, Method of locating metals and minerals in the ground.

Carlisle, D., and Cleveland, G.B. (1958), Spec. Rep. Div. Mines Calif., No. 50, 31p, Plants as a guide to mineralisation.

Chan, K.M., and Riley, J.P. (1967), Analytica Chim. Acta. 39 103-113, Determination of tungsten in silicates and natural waters.

Clark, R.E.D. (1937), Analyst. 62 661-663, The colorimetric determination of tin by means of toluene -3,4-dithiol ("dithiol").

Clark, R.E.D. (1958), Analyst 83 396-402, o-Dithiols in analysis. Part VII. Toluene -3,4-dithiol as a general analytical reagent in qualitative analysis.

Cohen, N.E. (1969), Ph.D. Thesis, Massey University, New Zealand, Studies on the analytical geochemistry of uranium and associated elements in the Hawks Crag Breccia of New Zealand.

Davies, E.B., and Stockdill, S.M.J. (1956), Nature 178 866, A pasture response to sodium tungstate on a New Zealand soil.

Donati, A. (1927), Ann. chim. applicata 17 14-26, Spectrographic identification of some elements and the possibility of their detection by means of the arc spectrum. IV. Wolfram.

Feigl, F., and Krumholz, P. (1932), Angew. Chem. 45 674-675, Colorimetric determination of small amounts of tungsten.

Fer'yanchich, F.A. (1934), Zav. Lab. 3 301-303, Colorimetric determination of tungsten.

Fer'yanchich, F.A. (1937), Zav. Lab. 6 289-292, Colorimetric determination of tungsten and molybdenum.

Fisher, R.A., and Yates, F. (1957), Statistical tables for biological, agricultural and medical research, Oliver and Boyd, London.

Flinter, B.H. (1959), Am. Mineral. 44 738-751, The magnetic separation of some alluvial materials in Malaya.

Gilbert, T.W., Jr. (1956), Ph.D. Thesis, University of Minnesota, U.S.A.

Hamaguchi, H., Kuroda, R., Chimuzu, T., Isukahara, I., and Yakamoto, R. (1962), Geochim. Cosmochim. Acta. 26 503-505, Values for trace elements in G-1 and W-1 with neutron activation analysis. II. Molybdenum, tin, tantalum and tungsten.

Hamence, J.H. (1940), Analyst 65 152-154, A new test for the detection of molybdenum and tungsten.

Hawkes, H.E., and Webb, J.S. (1965), Geochemistry in Mineral Exploration. Harper and Row, N.Y.

Heimer, Y.M., Wray, J.L., and Filner, P. (1969), Plant Physiol. 44 1197-1199, The effect of tungstate on nitrate assimilation in higher plant tissues.

Hevesy, G.V., and Hobbie, R. (1933), Z. anorg. allgem. Chem. 212 134-144, Determination of molybdenum and tungsten in rocks.

Higgins, E.S., Richert, D.A., and Westerfield, W.W. (1956), Proc. Soc. Exptl. Biol. Med. 92 509-511, Tungstate antagonism of molybdate in Aspergillus niger.

Hobart, E.W., and Hurley, E.P. (1962), Analytica Chim. Acta 27 144-152, Spectrophotometric determination of molybdenum and tungsten in niobium with dithiol.

Hwang, J.C., and Doi, S. (1965), Hakko Kogaku Zasshi 41 474-480, Nitrogen fixing micro-organisms. III. Effects of some metals on the growth of nitrogen-fixing organisms.

Ivanova, G.F. (1968), Zh. Analit. Khim. 20 82-86, The role of chemical reactions in the electrode for increasing the sensitivity of the spectrographic determinations of molybdenum, tungsten and tin in rocks.

Jeffery, P.G. (1956), Analyst 81 104-109, The simultaneous photometric determination of molybdenum and tungsten in silicate rocks.

Kabiashvili, V.I. (1964), Soobshch. Akad. Nauk Georgian SSR 35 83-86, Biogeochemical significance of dispersed tungsten.

Kaufman, D., and Derderian, S.K. (1949), Anal. Chem. 21 613-616, Wolfram in low grade ores. Quantitative spectrographic determination.

Keeler, R.F., and Varner, J.E. (1957), Arch. Biochem. Biophys. 70 585-590, Tungstate as an antagonist of molybdate in Azotobacter vinelandii.

Keith, J.R. (1968), Prepr. Soc. Min. Eng. AIME, No. 68-L-320, 12p, Relationships of lead and zinc contents of trees and soils, Upper Mississippi Valley Districts.

Kleinhampl, F.J., and Koteff, C. (1960), Bull. U.S. Geol. Surv., No. 1085-C, 85-104, Botanical prospecting for uranium in the Circle Cliffs area, Garfield County, Utah.

Kovalevsky, A.L. (1966), Geokhimiya No. 6 737-744, Biogeochemistry of tungsten in plants.

Krylova, M.B. (1963), Dokl. Mosk. Sel'skokhoz. Akad. No. 89, 314-319, Tungsten and nitrogen fixation.

Malyuga, D.P. (1964), Biogeochemical methods of prospecting. Authorised translation from the Russian. Consultants Bureau, N.Y.

Mason, B. (1966), Principles of Geochemistry, John Wiley and Sons, N.Y.

Meggers, W.F., Corliss, C.H., and Scribner, B.F. (1961), NBS Monograph 32 - Part II, 272 p, Tables of spectral-line intensities.

Miller, C.C. (1941), J. Chem. Soc. 792, Preliminary observations on the behaviour of rhenium and molybdenum with toluene -3,4-dithiol.

Miller, C.C. (1943), J. Chem. Soc. 72-74, Qualitative semimicro-analysis with reference to Noyes and Bray's system: The aluminium group.

Miller, C.C. (1944), Analyst 69 109-112, Toluene -3,4-dithiol as a selective reagent for tungsten: The detection of tungsten, especially in molybdenum and rhenium compounds, and in ferrous alloys.

Miller, C.C., and Lowe, A.J. (1940), J. Chem. Soc. 1258-1263, Qualitative semimicro-analysis with reference to Noyes and Bray's system: the tantalum and the tungsten group.

Miller, R.B. (1963), N.Z.Jl. Sci. 6 365-377, Plant nutrients in hard beech. I. The immobilisation of nutrients.

Mitchell, R.L. (1960), J. Sci. Fd. Agric. No. 11 553-560, Contamination problems in soil and plant analysis.

Mitchell, R.L. (1964), Tech. Commun. Commonw. Bur. Soil Sci., No. 44A, 225 p, The spectrochemical analysis of soils, plants and related materials.

Nedler, V.V. (1940), Bull. acad. sci. U.R.S.S., ser Phys. 4 142-144, Influence of sample composition upon the accuracy of the quantitative spectral analysis of tungsten.

Nicholas, D.J.D., and Nason, A. (1955), Plant Physiol, 30 135-138, Role of molybdenum as a constituent of nitrate reductase from soybean leaves.

Norris, R.C. and Hjelm, H.F. (1961), J. exp. Educ., 29 261-270, Non-normality and product moment correlation.

North, A.A. (1956), Analyst 81 660-668, Geochemical field methods for the determination of tungsten and molybdenum in soils.

Norwitz, G., and Codell, M. (1954), Analytica Chim. Acta 11 359-366, Direct colorimetric determination of small amounts of tungsten in titanium.

Otteman, J. (1941), Investigation on the distribution of trace elements, particularly tin, in deep rocks and several rock-forming minerals of the Harz mountains, Z. angew. Mineral 3 142-6.

Raikhbaum, Y.D. (1939), Zavod. Lab. 8 601-605, Determination of wolfram in minerals by the comparison of spectral energies.

Rankama, K., and Sahama, Th.G (1950), Geochemistry, Univ. Chicago Press, Chicago.

Romney, E.M., and Rhoads, W.A. (1966), Soil Sci. Soc. Amer. Proc. 3 770-773, Neutron activation products from project sedan in plants and soils.

Sandell, E.B. (1946), Ind. Eng. Chem. Anal. Ed. 18 163-167, Determination of tungsten in silicate rocks.

Scobie, A.G. (1943), Ind. Eng. Chem., Anal. Ed. 15 79-80, Spectrochemical assay for traces of tungsten.

Sergeev, E.A. (1947), Zavods. Lab. 13 231-233, A method for exciting spectra in the arc, with the super-position of an electric field.

Severne, B.C. (1972), Ph.D. Thesis, Massey University, New Zealand, Botanical methods for mineral exploration in Western Australia.

Stanton, R.E. (1970), Proc. Australas. Inst. Min. Metall. No. 236 59-60, The colorimetric determinations of tungsten in soils, sediments and rocks by zinc dithiol.

Stary, J. (1964), The Solvent Extraction of Metal Chelates, Pergamon Press, Oxford.

Stevenson, G. (1953), Ann. Bot. (London), 17 342-345, Bacterial symbiosis by some New Zealand plants.

Taka hashi, H., and Nason, A. (1957), Biochim. Biophys. Acta 23 433-434, Tungstate as a competitive inhibitor of molybdate in nitrate assimilation and in nitrogen fixation by Azotobacter.

Tennant, C.B., and White, M.L. (1959), Econ. Geol. 54 1281-1290, Study of the distribution of some geochemical data.

Timperley, M.H. (1971), Ph.D. Thesis, Massey University, New Zealand Biogeochemical studies of nickel and copper in New Zealand.

Timperley, M.H., Brooks, R.R., and Petersen, P.H. (1972), Proc. Australas. Inst. Min. Metall. No. 242 25-36, The improved detection of geochemical soil anomalies by multiple regression analysis of biogeochemical data.

Vinogradov, A.P. (1954), Trudy Biogeokhim Lab., Akad. Nauk SSSR 10 3-27, Search for ore deposits by means of plants and soils.

Ward, F.N. (1951), Anal. Chem. 23 788-791, Determination of molybdenum in soils and rocks. A geochemical semimicro field method.

Warren, H.V., Delavault, R.E., and Fortesue, J.A.C. (1955), Bull. Geol. Soc. Am. 66 229-238, Sampling in biogeochemistry.

Wells, J.E., and Pemberton, R. (1947), Analyst 72 185-188, The microchemical determination of molybdenum in steel.

Williams, X.K. (1967), N.Z. Jl. Geol. and Geophys. 10 771-797, Statistics in the interpretation of geochemical data.

Wilson, S.H., and Fieldes, M. (1944), Analyst 69 12-13, Combined chemical and spectrographic method for the determination of traces of wolfram in rocks.

Wood, D.R., and Clark, R.T. (1958), Analyst 83 326-334, Determination of tungsten in titanium, zirconium, and their alloys.

PUBLICATIONS ARISING FROM THIS THESIS

Quin, B.F., and Brooks, R.R. (1972), Analytica Chim. Acta. 58 301-309, The rapid determination of tungsten in soils, stream sediments, rocks and vegetation.

Quin, B.F., Brooks, R.R., and Reay, P.F. (1972), Pl. Soil. 36 (in press), Short Communication: The uptake of tungsten by Nothofagus menziesii.

Quin, B.F., and Brooks, R.R. (1972-3), N.Z. Jl. Sci. (in press), The tungsten content of some plants from a mineralised area in New Zealand.

Quin, B.F., and Brooks, R.R. (1973), Geochemical and biogeochemical studies of tungsten in New Zealand. To be submitted to N.Z. Jl. Sci.

ACKNOWLEDGEMENTS

I would like to thank Dr R.R. Brooks for his enthusiastic encouragement and assistance during the course of the work summarised in this thesis, and the time he spent in this.

I am indebted to Carpentaria Exploration Ltd for extensive financial and logistic support during the investigations at Barrytown, and in particular I would like to thank Mr J.A.C. Painter and Mr R.M.S. Lee of this company for their assistance.

Thanks to Dr M.H. Timperley for his assistance with the statistical treatment of the data, and for the use of his computer programme.

To Dr P.F. Reay of the Applied Biochemistry Division, D.S.I.R., for his supervision of the tungsten uptake experiment.

And finally to various members of the University staff, including Dr J. Ogden and Dr J.P. Skipworth of the Botany and Zoology Department, Dr J.H. Kirkman of the Soil Science Department, and Dr G.G. Pritchard of the Chemistry, Biochemistry and Biophysics Department for their helpful advice on various aspects of this work.