

Copyright is owned by the Author of the thesis. Permission is given for a copy to be downloaded by an individual for the purpose of research and private study only. The thesis may not be reproduced elsewhere without the permission of the Author.

BIOGEOCHEMICAL STUDIES  
OF  
NICKEL AND COPPER  
IN  
NEW ZEALAND

A thesis presented in partial fulfilment  
of the requirements for the degree  
of Doctor of Philosophy  
at  
Massey University

Michael Horace Timperley

1971

ABSTRACT

The accumulations of various metals by some indigenous trees growing on the Riwaka Basic Complex, North-west Nelson, New Zealand, were investigated by the application of statistical techniques to biogeochemical data. Particular reference was given to nickel and copper to evaluate the usefulness of plant analysis as a prospecting tool.

Preliminary investigations showed that serious errors could result from the methods of sampling plants and soils and sampling procedures were adopted to minimise these errors. In addition, errors arising from atomic absorption analysis were found to be significant for some metals.

Leaves and twigs from three Nothofagus species, N. racemosa and N. acutifolia as well as their associated soils, were collected and analysed for nickel, cobalt, copper, zinc, chromium, calcium, magnesium, manganese and potassium. The plants were also analysed for iron. These results showed that each species accumulated different, but related, amounts of various metals and that they distributed these metals in different ways between their leaves and twigs.

N. truncata and N. fusca which are closely related genetically, accumulated metals to similar degrees, while N. menziesii which is not closely related to the other Nothofagus species accumulated metals to differing degrees.

Relationships between the metal concentrations in the plants and in the soils were evaluated by computing correlation coefficients. The best correlations for nickel were obtained for the Nothofagus genus although the other species also showed highly significant correlations. The Nothofagus genus also showed the best correlation for copper.

In view of the above results, a more extensive study of the Nothofagus genus was carried out. A second survey was undertaken in the same area in which leaf samples of this genus as well as their associated soils were collected. While the metal concentrations in the soils collected in this survey compared well to those collected previously, the metal concentrations in the plants, in general, did not show good agreement.

Trend analysis was used to compare in detail the nickel and copper contents in the leaves of the Nothofagus genus with the concentrations of these metals in the soils. It was shown by comparison of the trend surfaces and residuals that the accumulation of nickel was determined primarily by the concentration of nickel in the soil, whereas for copper the accumulation by the plant was a function primarily of the specific requirement of the plant for this metal.

Multiple regression analysis was used to improve the prediction of the copper and nickel concentrations in the soil from the concentrations of these metals in the leaves of the Nothofagus species, by making quantitative allowance for the processes influencing the

accumulation of these metals by the plants. Improvements of between 25% and 35% were obtained at the 90% confidence level.

Inter-metal ratios in the leaves were considered as possible indicators of nickel and copper concentrations in the soil but the results were discouraging.

Studies were made of the locations and chemical forms of nickel, copper, zinc and iron in both freeze-dried and fresh leaves from some trees growing on the Complex. Atomic absorption spectrophotometry was used to measure the concentrations of these metals in both plant extracts and on the electrophoresis and chromatography papers used to separate the metal complexes in the extracts. Results indicated that the major part of the nickel present in the leaves was not contained in cell organelles nor was it bound to cell walls, but existed as a positively charged complex in either the cytoplasm and/or the vacuole. Copper, zinc and iron were distributed differently with varying fractions, depending on the metal, existing predominately as anionic complexes.

It was concluded that the research embodied in this thesis had illustrated the application of statistical techniques to biogeochemical studies, showed that biogeochemical prospecting for nickel in New Zealand was feasible and that methods of total analysis for metals could be applied to the study of microgram amounts of metals in biological systems.

### ACKNOWLEDGEMENTS

The author would like to thank his supervisors Dr. R. R. Brooks and Dr. P. J. Peterson for their valuable advice and assistance during the course of this project.

To the staff of the computer unit, the author extends his thanks for the many helpful suggestions during the writing of the computer programmes.

He also wishes to thank Mrs Dawn Mansford for typing the thesis and his wife, Helen, for assistance with the diagrams.

The author is most grateful to the Mineral Resources Subcommittee of the New Zealand Grants Committee for finance to support this project and also to the former McIntyre Mines (N.Z.) Ltd. for assistance with transport and accommodation in the field.

TABLE OF CONTENTS

	<u>Page No.</u>
ABSTRACT	ii
ACKNOWLEDGEMENTS	v
TABLE OF CONTENTS	vi
LIST OF FIGURES	xi
LIST OF TABLES	xiii
SECTION I - GENERAL INTRODUCTION	1
SECTION II - ANALYTICAL TECHNIQUES	16
A. Instruments and Chemicals.	17
B. Sensitivities and Limits of Measurement.	18
C. Treatment of Plant Samples.	21
1. Preliminary treatment	21
2. Ashing technique	21
3. Loss of metals during dry ashing	22
4. Dissolution and analytical technique adopted for plant samples	25
D. Treatment of Soil Samples.	26
1. Preliminary treatment	26
2. Dissolution procedure	26
E. Chemical and Spectral Interferences.	28
F. The Accuracy and Precision of the Dissolution and Analytical Methods for Plants and Soils and the Effects of these Parameters on Statistical Techniques.	29
1. Introduction	29
2. Precision	31
3. Accuracy	31
G. Measurement of Soil pH.	39
H. Statistical Procedures.	40
SECTION III - PRELIMINARY BIOGEOCHEMICAL SURVEY	41
A. The Sampling Grid.	42
B. Mineralisation within the Sampling Grid.	45
C. Vegetation Cover.	44
1. Introduction	44
2. Aerial photography	44
3. Ground survey	47

	Page No.
D. Evaluation of Plant and Soil Sampling Procedures.	49
1. Introduction	49
2. Leaves, twigs and trunk wood sampled from different heights	50
3. Samples from different depths in the soil	50
4. Variations of the metal concentrations in plants and soils over small distances	53
5. Discussion and conclusions	55
E. Statistical Treatment of the Data.	57
1. Correlation coefficients	57
2. The <u>reduced major axis</u> and graphing techniques	58
F. Preliminary Sampling Survey.	61
1. Metal concentrations in the leaves and twigs of the species sampled	61
2. The relationships between the metal concentrations in the plants and the soil	69
3. The three <u>Nothofagus</u> species	75
SECTION IV - MAJOR BIOGEOCHEMICAL SURVEY	81
A. Introduction.	82
B. The Precision of Geochemical and Biogeochemical Sampling.	85
1. Introduction	85
2. Results	85
3. Discussion	86
C. Further Comments on the three <u>Nothofagus</u> Species.	88
1. Introduction	88
2. Results	88
3. Discussion	94
D. The Relationships between the Metal Concentrations in the leaves of the <u>Nothofagus</u> Species and the Metal Concentrations in the soil.	97
1. Introduction	97
2. Preparation of soil fractions	97
3. Differences between the metal concentrations in the plants and in the various soil fractions	104
4. Correlation coefficients between the metal concentrations in the plants and in the various soil fractions	107

E.	The Use of Trend Analysis to Compare and Interpret Biogeochemical and Geochemical Data.	110
	1. Introduction	110
	2. Data distributions	115
	3. The application of trend analysis to the present study	116
F.	The Improved Prediction of Metal Concentrations in the Soil from the Metal Concentrations in the Leaf Ash.	125
	1. Introduction	125
	2. Multiple regression analysis	125
	3. The independent variables selected for regression analysis	126
	4. Distributions of the independent variables	127
	5. Procedure	128
	6. Results	128
	7. Discussion	131
	8. Conclusions	135
G.	The Effects of High Concentrations of Nickel and Copper in the Soil on the Metal Concentrations in the Leaves of the <u>Nothofagus</u> species.	138
	1. Introduction	138
	2. Inter-metal relationships within the leaves	139
	3. The influences of high nickel and copper concentrations in the soil on the metal concentrations in the leaves	142
	4. The influences of high nickel and copper concentrations in the soil on the ratios of the metal concentrations in the leaves	145
	5. Ratios of the metal concentrations in the leaves as indicators of soils containing high concentrations of copper	150
H.	Essential and Non-essential Trace Metals and how their nature affects Biogeochemical Prospecting Results.	154
	1. Introduction	154
	2. The use of data distributions	155
	3. The coefficients of variation	156
	4. The relative accumulation of a metal as a function of the total concentration of the metal in the soil	161



SECTION VI - SUMMARY AND GENERAL CONCLUSIONS	208
BIBLIOGRAPHY	213
APPENDICES	228
I Plant species recorded	229
II Frequency distributions of variables used in multiple regression analysis	231
III Correlation coefficient programme	232
A. Description of the programme	232
B. Programme listing	234
IV Stepwise regression analysis programme	238
A. Description of the programme	238
B. Summary of the essential procedures involved in each main programme	241
C. Programme listing	244
V Programme to compute the probability of site overlap	251
A. Description of the programme	251
B. Programme listing	252
VI Data listing	254
VII Publications arising from this thesis	289

LIST OF FIGURES

<u>Figure No.</u>		<u>After Page No.</u>
I - 1	Pathways of environmental movement of trace elements.	2
I - 2	The Geochemical Cycle.	10
I - 3	The Biogeochemical Cycle.	10
I - 4	Geological sketch map of the eastern part of North-west Nelson.	13
II - 1	Flowchart for plant and soil analysis.	25
II - 2	Apparent concentrations due to light scatter by the following metals: calcium, iron, magnesium, aluminium, potassium and sodium.	35
III - 1	The sampling grid.	42
III - 2	Soil profiles.	50
III - 3	Variations of the metal concentrations in plants and soils over small distances.	54
III - 4	Metal concentrations in the plants sampled.	61
III - 5	Iso-concentration contours of nickel in both the plants and soils.	73
III - 6	Iso-concentration contours of copper in both the <u>Nothofagus</u> spp. and the soil.	73
IV - 1	Relationships between the data collected in the March, 1969 and the November, 1969 sampling programmes.	36
IV - 2	Concentrations of metals extracted from soils by cold 1 M HCl as a function of time. Calcium, magnesium, nickel and copper.	102
IV - 3	Concentrations of metals extracted from soils by cold 1 M HCl as a function of time. Potassium, chromium and zinc.	102
IV - 4	Trend surfaces and iso-concentration contours of both the observed data and the positive autocorrelated residuals for nickel in the plants and soils.	117

<u>Figure No.</u>		<u>After Page No.</u>
IV - 5	Trend surfaces and iso-concentration contours of both the observed data and the positive autocorrelated residuals for copper in the plants and soils.	117
IV - 6	Concentrations in the <u>Nothofagus</u> spp. leaf ash and predicted concentrations in the soil (0.10 level of significance) plotted against the observed concentrations in the soil for nickel and copper.	133
IV - 7	Trend surfaces (0.05 level of significance) of the observed and predicted data.	133
IV - 8	Relative accumulation versus total soil concentration.	165
V - 1	Differential centrifugation scheme.	174
V - 2	Solvent extraction scheme for freeze-dried leaf tissue.	180
V - 3	Patterns of nickel after electrophoresis at pH 5.3 of the 80% aqueous ethanol leaf extracts.	187
V - 4	Patterns of some metals after electrophoresis at pH 5.3 of the aqueous extract of fresh <u>Q.acutifolia</u> leaves.	191
V - 5	Chromatography in butanol/acetic acid/water 12:3:5 of metal complexes isolated by preparative-scale electrophoresis.	195
V - 6	Gel filtration of the aqueous extract of fresh <u>Q.acutifolia</u> leaves.	198
V - 7	Patterns of nickel after electrophoresis at pH 5.3 of both the partially purified aqueous extract of fresh <u>Q.acutifolia</u> leaves and nickel cation standards.	201
V - 8	Chromatography of the partially purified aqueous extract from <u>Q.acutifolia</u> leaves. Patterns of nickel.	204
V - 9	Chromatography in ethanol/water 8:2 of the <u>Q.acutifolia</u> leaf extract.	204
Plate I	Aerial photograph showing the topography and vegetation cover in the vicinity of the sampling grid.	42
Plate II	Leaves from the trees sampled.	80

LIST OF TABLES

<u>Table No.</u>		<u>Page No.</u>
II - 1	Details of the analytical capabilities of the methods used.	20
II - 2	Percentage recoveries of 10 $\mu$ g each of nickel, copper and zinc after ashing at (a) 450°C and (b) 500°C for 12 hours in the presence of filter paper.	24
II - 3	Analysis of the standard diabase W - 1	32
III - 1	Metal concentrations in ash of leaves, twigs and trunk wood taken from different heights up two specimens of <u>Nothofagus fusca</u> .	51
III - 2	Total metal concentrations at different depths in the soil.	52
III - 3	Mean metal concentrations in the leaves and twigs of the plants sampled.	62
III - 4	Mean relative accumulations of the metals in the leaves and twigs of the plants sampled.	65
III - 5	Mean concentrations and concentration ranges of calcium, magnesium and potassium in the dry leaves of different trees.	63
III - 6	Correlation coefficients between the metal concentrations in the plants and in the soils.	71
III - 7	Mean metal concentrations in the leaves of the three <u>Nothofagus</u> species.	76
III - 8	Mean relative accumulations for the metals in the leaves of the three <u>Nothofagus</u> species.	77
III - 9	Mean relative accumulations for <u>N. truncata</u> and <u>N. menziesii</u> expressed relative to the values for <u>N. fusca</u> .	79
IV - 1	Mean metal concentrations in the plants and soils collected in March, 1969 and November, 1969.	84
IV - 2	Correlation coefficients between samples collected in March, 1969 and November, 1969.	85

<u>Table No.</u>		<u>Page No.</u>
IV - 3	Mean concentrations of some metals in the leaves of the three <u>Nothofagus</u> species collected in November, 1969.	89
IV - 4	Mean relative accumulations of some metals in the leaves of the three <u>Nothofagus</u> species collected in March, 1969, and November, 1969.	90
IV - 5	Mean metal concentrations in the dry leaves of the three <u>Nothofagus</u> species collected in March, 1969, and November, 1969.	92
IV - 6	Values of Students "t" for the difference in the percentage ash weights and the dry leaf concentrations of zinc and iron, between the three <u>Nothofagus</u> species.	95
IV - 7	Leaf length in relation to the mean relative accumulations of potassium and manganese in the dry leaves.	95
IV - 8	Analyses of a soil fraction at each stage of four successive passings through a 400 mesh brass sieve.	99
IV - 9	Mean metal concentrations in the leaf ash of the <u>Nothofagus</u> species and in the various soil fractions.	105
IV -10	Correlation coefficients between the metal concentrations in the leaves and the metal concentrations in the various soil fractions.	108
IV -11	Trend equations derived at the 0.05 level of significance.	118
IV -12	Results of regression analysis.	130
IV -13	Correlation coefficients for nickel and copper between the observed concentrations in the soil and both the predicted concentrations in the soil and the concentrations in the leaf ash.	134
IV -14	Significant ( $<0.001$ ) correlation coefficients ( $r$ ) between the metal concentrations in the leaves of the three <u>Nothofagus</u> species.	140

<u>Table No.</u>		<u>Page No.</u>
IV -15	Correlation coefficients between the metal concentrations in the leaf ash and the nickel and copper concentrations in the soil (-20 mesh).	145
IV -16	Correlation coefficients between the inter-metal ratios in the leaf ash of the three <u>Hothofagus</u> species and the nickel and copper concentrations in the soil (-120 mesh).	148
IV -17	The evaluation of inter-metal ratios in the leaf ash for indicating anomalous concentrations of copper in the soil.	152
IV -18	Ratios of the geometric and arithmetic means to the medians for various metals in different plant species.	157
IV -19	Coefficients of variation for some metal concentrations in the leaf ash of various plant species and their associated soils.	159
IV -20	Correlation coefficients between the relative accumulations and the total metal concentrations in the soil.	162
V - 1	Details of the leaf samples used in the study of the metal complexes in leaves.	172
V - 2	Percentage distributions of some metals in the fractions obtained by differential centrifugation.	177
V - 3	Percentage distributions of nickel in the freeze-dried leaves among the various solvent extracts.	182