Plant-available elements in soils and their influence on the vegetation over ultramafic ("serpentine") rocks in New Zealand

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Ultramafic ("serpentine") soils from the Nelson Region contain low total levels of calcium, potassium, phosphate and high total levels of chromium, cobalt, iron, magnesium, manganese and nickel. However, the plant-available fraction as measured by extraction procedures, differs considerably from the total elemental abundances in the soils. The solubility of individual elements is unrelated to total abundance in the soil. Only extractable manganese and iron could be predicted by their total concentration. Extraction experiments indicated that chromium and cobalt have low solubility in the pH range to which serpentine plants are exposed and therefore unlikely to be toxic. Soil analyses across a sedimentary/ultramafic soil boundary indicated that higher levels of extractable nickel and/or magnesium in ultramafic soils seem likely to account for the observed vegetation change. The pH of soils under beech forest was significantly lower than that under serpentine vegetation and was probably a result of humic decay of forest litter. Nickel availability increases with decreasing pH. This effect is not limiting on nickel-poor sedimentary soils, but the increased nickel availability at lower pH on serpentine soils may prohibit forest colonisation of this ultramafic environment. This hypothesis is supported by the observation that isolated Nothofagus and Pinus radiata have colonised humus-deficient ultramafics at Hackett Creek and the Cobb asbestos mine.

Keywords: Serpentine flora; nickel; Dun Mountain; New Zealand; serpentine soils

INTRODUCTION

Ultramafic ("serpentine") rocks are formed when sections of the upper mantle become exposed at the surface of the earth due to tectonic movement. These rocks are rich in the minerals olivine and pyroxene which weather to give a variety of soils known collectively as ultramafic or serpentine (Brooks 1987). Geologically the word "serpentine" refers to a mineral rather than a rock type, but is applied by ecologists to include ecosystems associated with all ultramafic rocks. Such rocks may be found at several sites in Northland, Nelson Province and Otago (Coombs et al. 1976).

Characteristics that typify serpentine soils (Brooks 1987) are: (1) they contain predominantly ferromagnesian minerals, the silica and magnesium content decreasing as the soils are weathered; (2) they contain relatively large concentrations of nickel, chromium, manganese and cobalt; (3) they have relatively low concentrations of nitrogen, phosphorus and potassium; (4) they have a high magnesium/calcium quotient; (5) they have a low organic matter content; (6) they are sandy, relatively homogeneous, and generally shallow with a typical depth of 150 mm of soil on top.

Outcrops of ultramafic rocks nearly always support a characteristic vegetation, distinct from adjacent areas. The vegetation boundary between ultramafic and non-ultramafic soils is

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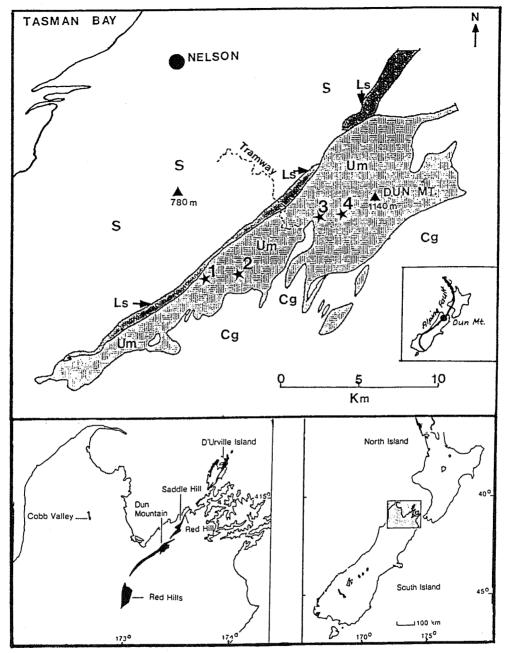


Fig. 1 Map of the Dun Mountain Ophiolitic Belt. Cg-Patuki Melange of a conglomerate of sedimentary, volcanic and ultramafic rocks. Ls-Wooded Peak Limestone consisting of poorly bedded grey limestone with with lenses of grey siltstone. S-Greville Formation of interbedded laminated grey sandstone, siltstone and mudstone. Um-Layered dunite, harzburgite and pyroxenite with widespread serpentinisation. 1-Hackett Creek chromite mine: 2-United Mine: 3-Site of sedimentary conglomerate/ultramafic ecotone transect (Fig.6): 4-Dun Saddle.

often sharp, coinciding with the geological contact and visible over only a few metres. The Dun Mountain Belt is a particularly good example of this sharp differentiation (Fig.2). There is much debate concerning why serpentine areas have such a distinctive stunted flora. The nature of the so-called "serpentine factor" (Krause 1958; Kinzel 1982) has been sought by looking for consistent chemical and physical characteristics of soils that either individually or collectively allow for the development of "serpentine floras" throughout the world (Brooks 1987; Kinzel 1982). Suggested factors influencing the development of "serpentine floras" are: (1) the toxic effects of nickel, chromium, cobalt, and manganese; (2) the toxic effect of magnesium at very high concentrations; (3) the very high magnesium/calcium quotient causing inhibition of calcium uptake; (4) the low soil concentrations of available plant-essential macronutrients; (5) the unfavourable physical nature of the soil (sandy, shallow and susceptible to erosion – Jørgensen 1974) and; (6) a combination of some or all of the above. The large variation in chemical composition within, and between, ultramafic soils from different geographical areas, suggests that there is no single underlying "serpentine factor" common to all areas.

Some previous studies of plant/soil relationships in serpentine floras have concentrated on the *total* metal content of the soils rather than the *plant-available* fraction (Krause 1958). We follow the more logical approach that the availabilities of soil constituents are more relevant than their totalities when considering what possible edaphic factors could control a serpentine flora. The objectives of our studies reported below, are: (1) to present data on the chemical composition of ultramafic soils from the Nelson area; (2) to compare total elemental concentrations with extracts simulating the plant-available fraction; (3) to examine changes in the total and extractable fractions across an ecotone; (4) to relate soil composition to the composition and physiognomy of the overlying vegetation.

THE STUDY AREA

Geology

The Dun Mountain Ophiolitic ("Mineral") Belt in Nelson Province is the type locality for dunite (FeMgSiO₄) first described by Hochstetter at Dun Mountain last Century (Bell et al. 1911).

The belt (Fig.1) extends southwards from d'Urville Island through Saddle Hill and the Dun Mountain to Red Hill in the Wairau Valley, where it is truncated by the Alpine Fault. The Dun Mountain Massif is situated some 13 km east of Nelson and rises to an altitude of 1129 m. The ultramafic rocks intrude the older surrounding sediments and volcanic rocks. The main rock types are dunite and harzburgite with a little pyroxene, and have a concentric serpentinization at the contacts with sediments and other ultramafic rock types.

Chrome and copper (mined at the turn of the century) are associated with a prominent fault near Wooded Peak. The surrounding non-ultramafic rocks are predominantly spilites interspersed in a Permian sedimentary sequence composed of greywackes, argillites and calcareous rocks (Lauder 1965).

Other mining activities were carried out at the United and Champion Mines in the Mineral Belt inland from Richmond along the United and Champion Creeks respectively. The primary ore was a mixture of pyrrhotite and chalcopyrite (Bell et al. 1911), and extensive cupriferous mine waste is still to be found at the abandoned United Mine site.

The Cobb Valley asbestos mine (Fig.1) is found in the Upper Takaka Valley. The deposits were mined from 1949 to 1963 (Williams 1965). All the ultramafic rocks are hydrothermally altered and the peridotitic differentiate has been completely serpentinised to chrysotile, bastite, and to an antigorite-like serpentine.

Vegetation and soils

Dun Mountain The vegetation of the Dun Mountain Belt (Fig. 2), with several endemic taxa, is floristically one of the most important of the ultramafic zones of New Zealand. The



Fig. 2 Vegetational boundary between ultramafic (scrub) and sedimentary/ultramafic (forested) soils on the south slope of Dun Mountain.

vegetation has been described by Lee (1980,1992) who recognised several distinct communities:

- (1) **Mixed beech forest** dominated by *Nothofagus fusca* with associated *N.menziesii*, *N.solandri* var. *cliffortioides*, and *Podocarpus hallii* reaching a canopy height of 23 m on sedimentary rocks of Wells's Peak.
- (2) **Transition forest** between ultramafics and sedimentaries consisting of a low tree assemblage of variable composition depending on the predominance of one or more parent materials in the soil. The canopy is dominated by *Nothofagus solandri* var. *cliffortioides*.
- (3) Leptospermum scoparium shrubland forms a large part of the serpentine vegetation and includes serpentine endemics such as *Pimelea suteri* and *Myosotis monroi*. A small herb, *Notothlaspi australe*, is often found in damper places. The small gentian *Gentiana corymbifera* is also very common as a coloniser of serpentine scree. Larger shrubs include *Hebe odora* and *Cassinia vauvilliersii*.
- (4) *Chionochloa* tussock grassland typical of the open vegetation of the dunites and peridotites of the Dun Mountain Massif, increases in importance with altitude.

Cobb Valley The vegetation of the Cobb asbestos mine tailings is exceedingly sparse. On the slopes it is confined to *Colobanthus strictus* and a dwarf tussock grass (*Poa* sp.). In the flat areas below the tailings, there is an occasional *Nothofagus* (Fig.3).

The soils of the Dun Mountain Ophiolitic Belt are quite variable but were originally classified as "Dun Steepland" (Chittenden et al. 1966). A soil profile in the Lee Valley under stunted manuka and native grasses (15° slope) was described as follows:

(1) 2.5 cm – dark brown sandy loam, friable, moderately developed fine soft crumb structure. (2) 12 cm – dark brown silt loam with rock fragments, friable, strongly developed medium nutty structure. (3) 22 cm – dark olive-brown silt loam with many rock fragments, friable, moderately developed medium granular structure. (4) Weathered serpentinite rock.

Elsewhere the soil cover consists of little more than weathered serpentine scree with little

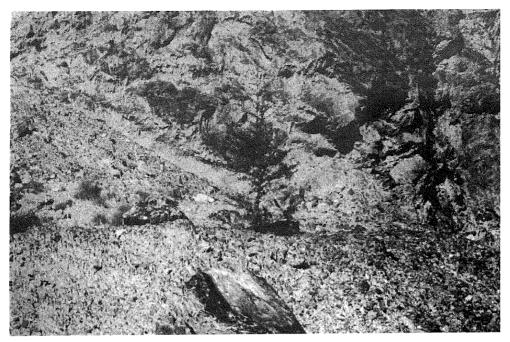


Fig. 3 Individual specimen of *Nothofagus solandri* colonising a patch of humus-deficient serpentine soil below asbestos tips at the Cobb Valley asbestos mine.

or no organic content. The modern nomenclature for this serpentine soil type is *magnesic mafic brown* (Anon 1992)

METHODS

Sampling and sample sites

Visits were made to Dun Mountain, United and Champion copper mines, Hackett chromite mine and Cobb Valley asbestos mine and to the ultramafic terrain surrounding these areas (Fig. 1). Soils were collected from each site and samples were taken from the material immediately under the usually sparse layer of humus and surface litter at a depth of about 10 cm. These samples were composites of about 5 different samples.

At Coppermine saddle near the Dun Mountain, a transect was located across a beech forest/serpentine scrub ecotone over a soil boundary. The position of the transect was determined by selection of a site with horizontal flat topography free of downslope movement of material and where a sharp vegetation boundary was observed. From X-ray diffraction studies it was established that the beech forest overlies a sedimentary/ultramafic melange dominated by talc and quartz. The scrub covers a typical ultramafic assemblage of antigorite and magnetite. The transect was 30 m in length, and extended 15 m into each soil type. Along the transect, soil samples were collected every 2 m and represented a composite of three individual samples taken on a parallel line at right angles to the direction of the transect. The samples were taken immediately below the forest litter at depths ranging from about 20 cm in the forest to 10 cm over the open ultramafic terrain.

Methods of sample treatment

All soils were sieved to -70 mesh (0.2 mm) size and 0.5 g subsamples were weighed into polypropylene cups. Twelve mL of 1:1 HF/HNO₃ was added to each cup and the solutions were evaporated to dryness on a water bath. Then 12 mL of 2M HCl was added to each cup and the solutions warmed to redissolve the material. The chemical elements in solution were

determined by flame atomic absorption spectrometry (FAAS). To measure the pH of the soils, 2.5 mL of water was added to 1 g of sieved soil and the mixture left overnight before measurement with a pH meter. A total elemental analysis by X-ray fluorescence spectrometry was also performed.

The question of what extractant should be used to simulate the plant-available fraction of metals in soils has received a great deal of attention without any real consensus. The pH of the soil in the rhizosphere of plants is often up to 2 pH units more acidic than the bulk soil, and this difference is greater at high soil pH values (Salisbury & Ross 1978). The pH values of the soil samples taken in this survey ranged from 4.4 (mean 4.9) under forest litter to 7.7 (mean 7.1) under serpentine scrub (the majority of the samples). It was decided that extractants at pH 4.6, and 5.9 would simulate the conditions to which the plants are exposed on all these soils. Extractions at pH 7.0 were also carried out for comparison purposes. The pH value of 5.9 was about 2 units below the pH of serpentine soils, and after further experimentation (see below) was considered to be overall the most suitable for extraction studies to determine the plant-available fraction of elements in the soils.

There was a further rationale for selection of pH 5.9 as the one most likely to simulate uptake of elements from the soils. In an experiment, the serpentine-endemic Italian crucifer *Alyssum bertolonii* was grown for three months in serpentine soil from the Dun Mountain complex. This soil contained a total of 6090 μ g/g Ni (Table 1). The plants had been sown in a tray containing 3.46 kg of soil and extracted 0.019 g of nickel. This represented an extraction of 5.5 μ g/g of this metal. The rhizosphere of plants is usually in contact with only 0.4–2.8 % (by volume) of the surrounding soil (Barber 1984). If soil interception were the only factor involved in element uptake by plants, the total available nickel in the soil should therefore be in the range 196–1375 μ g/g. This figure is however far too high, because it does not take into account the mass flow and diffusion (Barber 1984) that on average amount to ten times the root interception factor. If this combined figure is taken (i.e. 4–28%), the plant experiments indicate a probable 20–138 μ g/g extractable nickel with a mean of 79 μ g/g. Our experimental value using KH phthalate at pH 5.9 was 84 μ g/g Ni (Table 2).

Extractions in the range pH 1–9 were performed on a bulk quantity of serpentine soil collected from near the United Mine (Table 3). Such a range extended well outside that which would represent a plant-extractable fraction for individual elements, but it was selected to give a complete picture of potential extractability over the entire range. We decided to use NH₄OAc and buffered KH phthalate to investigate the plant-available elements from the other soils of the ophiolitic complex (see Table 4) at pH 4.6, 5.9 and 7.0.

The extractable fraction of soil elements was determined by adding 10 mL of extractant to 0.5 g of soil. The mixtures were shaken overnight and the supernatant decanted. The extracts were analysed by FAAS.

RESULTS AND DISCUSSION

The chemical composition of the soil examined (Table 1) is consistent with the general chemical properties of a serpentine soil described in the introduction. The salient characteristics

Table 1 Elemental concentrations (%) in a typical serpentine soil of the Nelson region. Notes: (1) analyses performed by X-ray fluorescence spectrometry; (2) soil from Serpentine Rd between Rai Valley and Nelson; (3) values in parentheses are mean values for non-serpentine soils (Brooks 1987).

Al	1.53 (6.03)	Ca	0.262 (1.15)	Co	0.054 (0.005)	Cl	0.013 (0.02)
Cr	0.785 (0.001)	Cu	0.010 (0.0005)	Fe	23.42 (2.68)	K	0.017 (1.49)
Mg	15.92 (0.55)	Mn	0.278 (0.12)	Na	0.009 (0.10)	Ni	0.609 (0.001)
O	41.5 (55.08)	P	0.034 (0.074)	S	0.052 (0.056)	Si	15.7 (32.35)
Ti	0.013 (0.30)	V	0.002 (0.01)	Zn	0.014 (0.015)	Total	100.2 (100.0)

Table 2 Statistical analysis (t – tests) of elemental concentration (μg/g unless otherwise stated) in soils as a function of distance across an ecotone over a sedimentary ultramafic soil boundary. Notes: S** = very highly significant (P < 0.001), S = significant (0.01<P < 0.05), NS = not significant (P > 0.05). †extracted with NH₄OAc at pH 7.0, †extracted with KH phthalate/NaOH at pH 5.9, ††extracted with KH phthalate/NaOH at pH 4.6.

Vari- able	Sedi- mentary mean	Ultra- mafic mean	P	Signifi cance
pН	4.9	6.6	< 0.001	S**
Al	4.6%	0.23%	< 0.001	S**
Ca	2500	3000	0.87	NS
Ca^{\dagger}	450	1190	0.012	S
Ca ^{††}	160	420	0.043	S
Ca ^{†††}	120	340	0.21	NS
Co	39	268	< 0.001	S**
Cr	302	2490	< 0.001	S**
Cu	43	33	0.68	NS
Fe	4.03%	17.3%	< 0.001	S**
$Fe^{\dagger\dagger}$	549	9.2	0.027	S
$Fe^{\dagger\dagger\dagger}$	285	74	0.007	S**
K	308	1509	< 0.001	S**
Mg	4.2%	12.1%	< 0.001	S**
Mg^{\dagger}	429	1755	< 0.001	S**
Mg ^{††}	370	1942	< 0.001	S**
Mg†††	274	1875	0.0015	S*
Mn	678	4250	< 0.001	S**
Mn^{\dagger}	38	18	0.11	NS
$Mn^{\dagger\dagger}$	64	33	0.175	NS
$Mn^{\dagger\dagger\dagger}$	1.69	1.74	0.0017	S*
Ni	288	2259	< 0.001	S**
Ni [†]	3.9	19.3	< 0.001	S**
Ni ^{††}	4.8	53.6	< 0.001	S**
Ni ^{†††}	7.4	93	< 0.001	S**
PO_4	0.6	0.8	0.55	NS
Zn ⁴	55	91 .	0.047	S

of the soil are the very high magnesium/calcium quotient of 61 (Brooks 1987 quotes 23 for the mean of 7 serpentine soils worldwide) and the high concentrations of elements of the iron family such as chromium, cobalt, manganese and nickel. The essential plant micronutrients such as potassium and phosphorus also have very low concentrations in this material, and the molybdenum content was below the detection limit.

The toxicity of an element to plant growth depends on its nature and its availability in the soil rather than on its total concentration. Figures 4 and 5 show the extractability at different pH levels, of some elements in the same soil described in Table 1. These figures show that the elements that make up a large proportion of the soil do not necessarily form a similarly large proportion of the available elements. Magnesium is the most available metal in this soil, followed in decreasing order by iron, calcium, nickel, manganese, cobalt, copper, zinc and chromium. Magnesium, nickel and manganese were available at concentrations above those shown to be toxic to most plants (Proctor 1970; Robertson 1985). The availability of all transition metals increased exponentially as the extractant became more acid.

Fig. 4 shows that there is a large excess of extractable magnesium over calcium, of the order of 20:1 (Fig.4). In non-serpentine soils the quotient is typically 1.0 (Brooks 1987). The magnesium/calcium quotient decreased from pH 1 to pH 4 then increased from pH 4 to pH 7. The extractabilities of Ni, Mn, Co, Cr and Zn increased exponentially with lower pH values (Fig. 5).

The chemical compositions of all the soils tested were similar to that of a typical serpentine soil, with the exception of soils from the United Mine, which were high in copper and soils

Table 3 Extractants used to measure available elemental concentrations in soils. Note: the natural pH of the soil was 7.5

pН	Extractant	pН	Extractant	
1.0	0.2M HCl	2.3	KH phthalate/HCl	
3.2	KH phthalate/HCl	4.2	KH phthalate/NaOH	
5.2	KH phthalate/NaOH	5.3	1M NH ₄ NO ₃	
5.9	0.05M CaCl,	6.2	KH phthalate/NaOH	
6.3	$0.1M \text{ NaNO}_3^2$	7.0	1M NH₄OAc	
8.5	H ₃ BO ₃ /KCl ³	9.0	H₃BO₃/ᢜCl	

from United Valley and Cobb Mine which were low in chromium (Table 4). The growth of stress-tolerant plants such as *Cyathodes juniperina*, *Leptospermum scoparium* and *Pteridium esculentum* on the waste material from the United Mine is strong evidence of its infertility.

The very low concentrations of extractable chromium, as well as the presence of very stunted serpentine vegetation in the United Valley and Cobb Asbestos Mine, where soils are low in chromium, indicate that chromium is not important in controlling vegetation on ultramafic areas. Serpentine plants, without exception, contain only trace quantities of this element (Brooks 1987). Similarly, the recorded levels of extractable copper, zinc and cobalt were below 0.1 µg/g even using the most acidic extractant (pH 4.6), indicating that these elements are unlikely to be toxic to plant growth.

The concentration of extractable iron was very low compared with its total concentration in the soil. In many cases it was lower than extractable nickel. At pH 7, the concentration of extractable iron in all the soils tested was below the detection limit $(0.1 \,\mu\text{g/g})$, suggesting that plants growing over iron-rich ultramafic soils can actually suffer from an iron deficiency because of the exceeding low availability of iron to plants at higher pH values.

The concentrations of total soil nickel, chromium, manganese and cobalt all showed significant increases with distance into the ultramafics across an ecotone near the Dun saddle

Table 4 Mean elemental content (total and extractable) of some ultramafic soils taken from around the Nelson region. All values are in $\mu g/g$ unless otherwise indicated. *extracted with NH₄OAc at pH 7.0; **extracted with KH phthalate at pH 5.9; **extracted with KH phthalate at pH 4.6.

	Dun Mountain (n=5)	Dun Saddle (n=3)	Cobb Mine (n=5)	United Mine (n=8)	United Valley (n=2)
pН	6.9	7.4	7.7	6.0	7.5
Al	6036	1001	576	2931	697
Ca	1553	11316	226	2946	963
Ca*	457	279	46	318	123
Ca**	203	142	14.9	99	143
Ca***	197	147	18.7	_	372
Co	222	190	121	112	391
Cr	892	3151	536	456	589
Cu	59	29	11.0	3101	107
Cu*	_	_	_	90	_
Cu**	_	_	_	314	_
Fe(%)	22.6	13.0	4.9	21.5	29
Fe**	24.7	1.3	5.1	14.0	8.4
Fe***	61.2	70	24	.	61
K	1682	1735	773	1423	4831
Mg(%)	7.3	18.0	19.1	11.5	16.7
Mg*	784	854	322	666	1520
Mg**	903	1005	408	765	1874
Mg***	825	1099	574		1977
Mn	1844	1708	395	624	3126
Mn*	6.9	2.4	0.6	3.7	5.4
Mn**	26	12.3	3.1	8.9	18.2
Mn***	61	30	120	****	65
Ni	2490	1505	2682	827	4713
Ni*	11.7	7.4	2.5	14.0	19.5
Vi**	27	28	7.6	38	42
Ni***	57	72	25	_	113
Zn	108	55	14.0	56	76

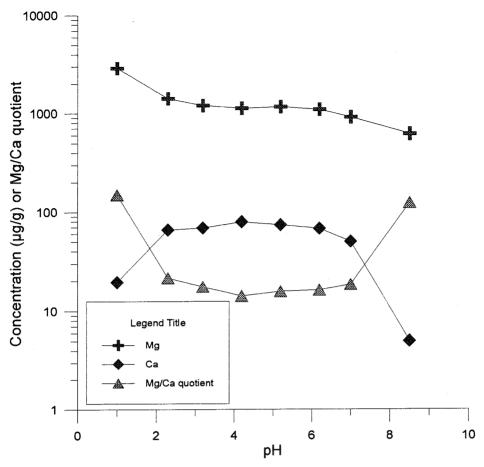


Fig. 4 Extractability of calcium and magnesium from a serpentine soil at various pH values.

(Fig.6). Abundance data for these and other elements are shown statistically in Table 2, which gives the level of significance for *t*-tests based on differences in the geometric means of the two populations. Apart from the four elements shown in Fig. 6, magnesium and total iron also showed a significant increase. There was no significant increase for calcium, copper, and phosphate, and a highly significant decrease in aluminium with distance across the transect. The same was true for extractable iron at pH 4.6 and 5.9. The latter can easily be explained from the effect of pH already shown in Table 2. In this transect the pH ranged from 4.4 under the *Nothofagus* forest to 7.2 under the serpentine scrub.

The results indicate that the toxic effects of chromium, cobalt and manganese are unlikely to be responsible for the vegetation change across the ecotone either because they are available in extremely low concentrations, or because they are not significantly greater in soil under the serpentine vegetation. The lack of a significant change in the concentrations of the plant nutrient phosphate, and the significant increase of available calcium across the ecotone, indicates that composition of vegetation on serpentine soil is not controlled by any deficiency of these elements. Surprisingly, the abundance of potassium was lower under the forest than in the ultramafic soil, even though both values were low compared with "normal" soils (Table 1). From Table 2 the most significant edaphic factors correlated with the distribution of the serpentine vegetation are an excess of available nickel and magnesium and/or an iron deficiency.

The concentration of extractable nickel at lower pH values (4.5-5.0: Fig. 7) increased and

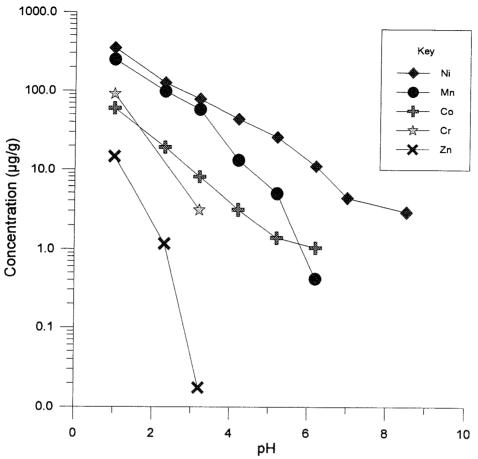


Fig. 5 Extractability of chromium, cobalt, manganese, nickel and zinc from a serpentine soil at various pH values.

may limit the establishment of beech forest on serpentine soil. When the beech species colonise the ecotone, humic acids generate a lower soil pH and increase the availability of nickel. This prevents further advance across this ecotone, implying that serpentine soils are unfavourable hosts for forest communities, rather than for individual species. This observation was endorsed by the presence of a specimen of *Nothofagus solandri* (Fig. 3) growing below the asbestos mine tip at the Cobb Mine. This individual plant will presumably continue to grow at the site until sufficient humus has accumulated to lower the pH to a level at which the extractable nickel will be toxic to the plant. A further piece of evidence to support this theory is afforded by the observation that in the ultramafics of the Hackett Creek area, individual, albeit stunted, specimens of *Pinus radiata* are able to survive, but only singly, and never as a group or clump. A similar pattern has been observed by one of us (R.R.B.) over the ultramafics of southeastern Spain where isolated specimens of *Pinus pinaster* are able to survive in an environment as equally hostile edaphically as the soils of the Dun Mountain Ophiolitic Belt.

It might be argued that serpentine scrub also produces an acidic litter. However, the production of this organic matter is far lower than under forest, and it is therefore likely that the rate of production will be more than counterbalanced by oxidation of the organic matter in the more open environment of serpentine vegetation. The above theory should be tested by growing individual forest species in serpentine soil where there is no litter to lower the pH.

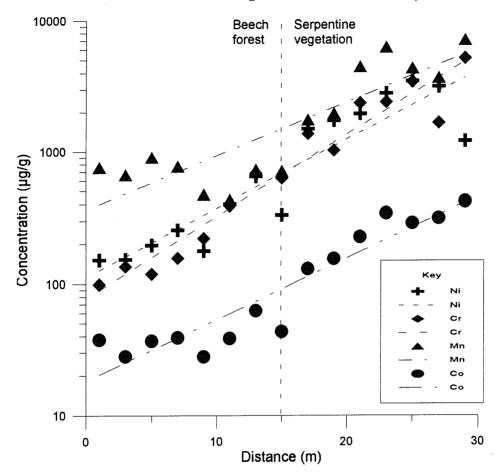


Fig. 6 Total abundances of chromium, cobalt, manganese and nickel in an ecotone across a sedimentary/ultramafic soil boundary.

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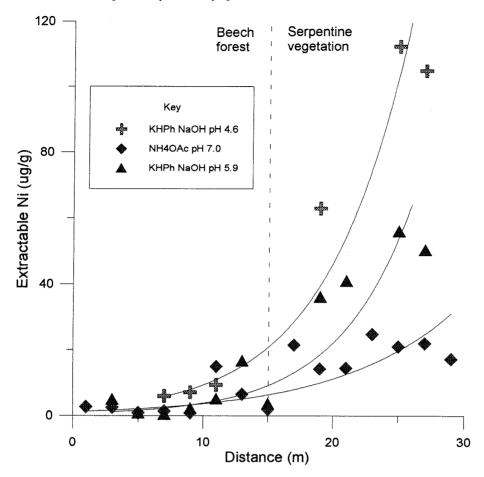


Fig. 7 Extractability of nickel at different pH values across an ecotone over sedimentary conglomerate/ultramafic soil boundary.

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