BIOGEOCHEMICAL STUDIES ON SOME NICKEL ACCUMULATING PLANTS FROM NEW ZEALAND AND NEW CALEDONIAN SERPENTINE AREAS.

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ABSTRACT

Serpentine areas in New Zealand and New Caledonia are described.

A study was made of soil factors controlling the distribution of five species from a serpentine flora in the Dun Mountain area, South Island, New Zealand.

Samples of soil were taken from sites of each of the species, and each sample was analysed for calcium, chromium, cobalt, copper, magnesium, manganese, nickel, potassium and zinc. On the basis of the species growing on them, the soil samples were divided into five groups: group 1, *Pimelea suteri*; group 2, *Myosotis monroi*; group 3, *Hebe odora*; group 4, *Cassinia vauvilliersii*; group 5, *Leptospermum scoparium*.

Discriminant analysis was used to characterise each group of soils on the basis of chemical composition. The results showed that the two endemic plants (*P. suteri* and *M. monroi*) were much more commonly found in localities of highest magnesium concentration. These two species were strongly differentiated by the potassium and copper levels in their soils. No strong elemental discrimination was found among the non-endemic species.

Correlation coefficients were calculated for the relationships between pairs of elements and highly-significant correlations ($P < 0.001$) are reported.

A nickel accumulating species from New Caledonia, *Homalium kanaliense* is compared with the New Zealand nickel accumulator, *Pimelea suteri*.

The very high accumulation of nickel in the New Caledonian species, presents interesting questions in plant physiology. Purification of nickel complexes from an aqueous extract of H. kanaliense leaves was achieved and preliminary identification methods employed. None of the nickel was associated with amino acids and the present evidence suggested possible complexing of the nickel to simple carboxyllic sugars.

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GENERAL
INTRODUCTION

Serpentine and other ultramafic soils through out the World are well known for their unique flora. These soils are easily differentiated from the surrounding lithology, with the 'boundary' lines clearly marked by the abrupt changes in vegetation type. Serpentine regions are typified by extensive areas of sparsely populated stunted vegetation with several species restricted exclusively to these areas with 'disjunctive distributions and boreal affinities' (Whittaker, 1954).

The general infertility of serpentine soils has been known for a long time. The cause of this infertility has been considerably disputed and is still largely unresolved, although it must be kept in mind that reasons applying to one serpentine area may not be applicable to others. However, from time to time, various hypotheses have been advanced to account for the characteristic flora of serpentine soils. They fall broadly into three categories.

Firstly, these soils are generally low in the plant nutrients; calcium, nitrogen, potassium, phosphorous, manganese and molybdenum. Secondly, the unfavourable calcium/magnesium ratio is regarded by many as the dominating factor. The magnesium content of many serpentine soils is often several times the calcium level.

Thirdly, the heavy metal content often approaches and exceeds toxicity levels, particularly those of nickel, chromium and cobolt.

Lipman (1926) has pointed out the unsatisfactory nature of the soil microflora as a possible cause of serpentine infertility.

In a review of some of the literature on this subject it can be seen that there are exponents of each of these hypotheses, with evidence obtained from work done on serpentine areas throughout the World.

At the beginning of the century, Loew and May (1901) showed that soils having a low calcium/magnesia ratio were much more infertile than high calcium soils. However, Gile (1913) considered that the other soil components were just as much of importance, if not more, as the calcium/magnesium ratio, and that in dilute soil solutions the influence of this ratio was even smaller.

From experiments carried out on the soils of the Great Dyke, Rhodesia, Blackshaw (1921) found that serpentine-derived soils were unproductive whilst soils derived from norite were made to be quite fertile. The serpentine-derived soils were high in magnesium and low in phosphorous and potassium, but large fertilizer applications did not achieve good results. Soane and Saunder (1959) substantiated these findings. Working again on Southern Rhodesian serpentine soils, the deficiency of nitrogen, phosphorous and potassium as the dominant cause of infertility was ruled out, in these areas anyway, because of the lack of response to heavy applications of fertilizers. They also discussed the effect of nickel and chromium toxicity, and possible interactions between chromium, phosphorous and calcium in the soil-plant system. Contradictory to this Gordon and Lipman (1926) concluded that serpentine infertility was caused by the low level of nitrogen, phosphorous and the alkaline reaction, and was not due to the low calcium/magnesium ratio.

The first workers to point out the role of high levels of heavy metals, were Robinson et al (1935), and they stated that this was the dominant cause of infertility. From a detailed physical analysis they also concluded that serpentine soils possess no physical characteristic which would render them particularly unfavourable for plant growth, although the clay content of some subsoils were high enough to impede drainage (This was noted in the Dun Mountain ultrabasic area). Birrell and Wright (1945) working in a New Caledonian serpentine area came to similar conclusions. They stated that nickel and chromium were responsible for the absence of the common tropical species, and 'species that have established themselves on the serpentine have developed sufficient tolerance to these elements to allow of a low, shrubby growth'.

Mitchell (1945) suggested that nickel was the limiting factor, and he indicated that the amount of nickel extracted by 2.5% acetic acid was the most representative of the nickel status. He put forward the value of 11 ppm soluble nickel which when exceeded would result in toxicity.

It has been found that a number of the Californian serpentine soils are deficient in available molybdenum (Walker 1948), but although Walker (1954) concluded that the molybdenum deficiency may contribute to the infertility of some serpentine soils, it is probably not the dominant factor. The same author suggested from his experimental evidence that the low calcium level is the basic cause of the peculiarity of serpentine soils, with the other factors of secondary importance. However low levels of plant nutrients, alkalinity, low available molybdenum, toxicity of nickel or chromium and the level of calcium and magnesium in the soil all have effect under certain circumstances. In some cases unfavourable physical aspects may also effect serpentine plant distributions.

Hunter and Vergnano (1952) reported that the infertility of serpentine soils at Whitecairns in Aberdeenshire was due to toxic levels of nickel. They found a low level of potassium, phosphorous and sometimes manganese, moderate levels of calcium and high levels of magnesium. The acetic acid-soluble nickel was very high. From experimentation with plant cultures the authors verified that plant growth decreased and necrotic symptoms increased when the calcium magnesium, nitrogen and potassium concentrations were low, and the nickel uptake was proportional to the acetic acid soluble content in the soil. They also compared chlorosis and necrosis due to nickel and cobalt, and while they were similar, they were not identical. Induced nickel symptoms were similar to those of plants with comparable nickel levels from serpentine areas. Cobalt symptoms of sand-cultured plants and necrosis of serpentine-grown plants were not comparable.

Hunter and Vergnano (1953) examined the activity of large amounts of heavy metals in producing chlorosis and other symptoms and found the order to be Ni > Cu > Co > Cr > Zn > Mo > Mn which compares well with the order of stability of metal complexes. Toxic effects of nickel, copper, zinc and manganese were associated with high concentrations of the elements in the leaf tissue, but this was not always so with chromium and aluminium. They suggested one factor in nickel toxicity may have been the inhibition of one or more of the functions of copper, as copper reduces the leaf necrosis produced by nickel, but not the nickel content of the leaf tissue.

Rune (1953) supported the hypothesis of Robinson *et al* (1935) that the high content of nickel and chromium was the general cause of infertility in serpentine soils but emphasized that the effect of the elements depended on soil factors such as low nutrient content, high magnesium, pH, mechanical composition etc. Other factors such as low competition, microclimate, topography, physical properties are important in determining the special characteristics of the serpentine flora. These may have varying effects in different areas.

Kruckeberg (1954) supported Walker's (1954) results in showing that tolerance of low calcium levels is a principal adaptation required by serpentine growing plants. He showed that serpentine plants adapted to low calcium, could grow equally well, if not better, on non-serpentine soils but intolerance to competition may have restricted them exclusively to serpentine areas. These results invalidated the ideas of Novak (1928) and Lammermayr (1927) who thought that serpentine plants were restricted to serpentine areas because of some essential requirement obtained only from those soils.

Whittaker (1954) described in detail a serpentine vegetation of the Sishiyou Mountains of South Western Oregon. He suggested three approaches to the problems of serpentines: the edaphic, the soil itself in relation to plant ecology; the autecological, which deals with the response of plant species to serpentine and non serpentine area; and the synecological, which considers the unusual character of serpentine vegetation. Comparing a diorite area with a serpentine vegetation he found that there were very few species that were found on both, and that many serpentine species have probably become serpentine endemics by a process of 'biotype depletion', through losing out in competition with other plants in non-serpentine populations.

Crooke et al (1954) working with sand and water cultures concluded that chlorosis depends on the nickel/iron ratio. The addition of iron lessened the toxicity of nickel and necrosis specifically caused by nickel was correlated with the nickel level in the leaves. This content was significantly reduced by a high concentration of iron in the nutrient solution. This confirms the view of Hunter and Vergnano (1953). Following a similar line Knight and Crooke (1956) studied the interaction between nickel and calcium and results showed how nickel may affect processes within the plant. It may be possible that organic acid metabolism may be affected in nickel toxic plants and that the state of solubility of copper in tissues may be altered by increased production of oxalic acid. They also showed that roots are damaged by nickel and the absorption and translocation of macronutrients is affected.

Soane and Saunder (1959) studing chromium and nickel toxicity in maize and tobacco found that the uptake of chromium in leaves was very slight, although severe root damage and accumulation of chromium in roots occurred. They hypothesized possible chromium, phosphorus and calcium interactions in the soil-plant system and because of this, chromium toxicity is less clearly evident than nickel toxicity. Also chromium is less readily transported to leaves by plants than is nickel.

In a comprehensive spectrographic survey Lounamaa (1956) compared fifteen trace elements in plants growing on silicic, calcareous and ultramafic rocks of Finland. The highest values for chromium, nickel and cobalt were obtained from plants growing on outcrops of ultramafic rocks. For ultrabasic soils he reported the following means (in p.p.m.); chromium 4000 ± 310, Nickel 1200 ± 190, Cobalt 140 ± 15, copper 22 ± 5.4, Manganese 1200 ± 150. Nickel was seldom observed to be below 1000 p.p.m. He also concluded that nickel and chromium were responsible for the peculiarities of ultrabasic flora.

Spence (1957) working with serpentine soils of the Island of Unst concluded that nickel is the cause of infertility only when associated with other factors such as soil instability and exposure. That is, the sparse colonization of the debris is due not entirely to a 'serpentine effect'. He noted that rapid weathering was associated with a high acetic acid-soluble nickel content.

Krause (1958), Paribok and Alexeyeva-Popova (1966), and Sarosick (1964) suggested that the survival of plants on serpentine soils was dependant on their ability to adapt to all of the factors operating in the serpentine ecosystem and not on one or several of these factors. These factors may operate in varying degrees and combinations depending on the local conditions.

Studing the toxicity and movement of heavy metals in Portuguese serpentine soils Menezes de Sequeira (1968) found that pH, organic matter, copper, nitrogen, potassium and other such factors have a profound effect on the degree of nickel toxicity. Accelerated soil erosion was a consequence of the scanty vegetation cover and detailed reconsideration of the weathering processes may be needed. The author concluded by agreeing with Krause's statement "we cannot mention a unique and omnipotent factor, for there are many serpentinic factors, that act in different ways and combinations depending on local conditions".

Proctor (1971) showed that Agrostis species growing in serpentine soils take up an excess of magnesium over calcium, but this excess is not obligatory for their survival. He showed that Agrostis species had a high tolerance of magnesium The importance of nickel and chromium was also studied. Grasses on serpentine soils were more tolerant to nickel than those grown on more calcarious soil. Proctor found that oats grown in a serpentine soil had a very large excess of magnesium and he considered that the cause of toxicity of this soil was primarily due to high magnesium levels in the presence of low calcium levels. He suggested that ecotype adaptation to this toxicity was widespread in British and Swedish serpentine soils.

Studies on Japanese serpentine soils have also been made. Takagishi et al (1974) have studied the abnormal features of mulberry plants growing on soils derived from serpentine.

Wiltshire (1973) studied the yields and the uptake and distribution of nickel between roots and shoots, measured in relation to changes in availability of nickel from soils resulting from fertilization with nitrates. Fertilization increased crop yields with nitrate fertilization decreasing the nickel content of shoots more than did the ammonium ion. The concentration of nickel in roots was greater in all treatments.

Lyon et al (1971) studied trace elements in a New Zealand serpentine flora and concluded that no universal mechanism could be applied to explain plant survival on a New Zealand serpentine soil, but differences were found between species in their ability to accumulate or exclude the various elements.

Ernst (1972) has undertaken ecophysiological studies of some heavy metal plants from South Central Africa, and found that the uptake of heavy metals depended on their availability in the soil. The uptake of heavy metals is specific for each species and within one species, for different tissues. Extractions of tissues of various plant parts showed that the binding of heavy metals within the cell was specific to the metal.

Shkol'nik and Smirnov (1972) experimenting with sunflower, showed that high concentrations of nickel and chromium induced certain morphological changes, such as dwarfism. They advanced the hypothesis that one of the main causes of morphological variations enduced by nickel and chromium is the increased R Nase activity leading to the destruction of nucleoli playing an important role in the preparation of cell divisions.

Ritter-Stadnicha (1972) made comparative studies of cell sap contents throughout the vegetation period on a number of plant species which occur on serpentine and calcium-rich soils. There was a general increase of magnesium, calcium and total free acids and oxalates throughout the vegetative period. The amount of total acids was higher in serpentine plants and the production of organic acids appeared to be stimulated by magnesium accumulation. Some species appeared to control the uptake of calcium and magnesium whilst others accumulated them randomly. The author concluded that the ability of individual species to grow on serpentine soils was a result of their physiological constitution.

So far little work has been done on the actual form of heavy metals such as nickel in the plant or how and why it is transported within the plant. Reilly et al (1970) has studied the accumulation and binding of copper in Becium homblii, whilst Tiffin (1971) has looked at the translocation of nickel in xylem exudate of plants but has not identified the nickel carrier.

Severne and Brooks (1971) have reported a high nickel accumulating plant, Hybanthus floribundus, growing on Western Australian ultrabasics and since then others have been found in New Caledonia. (Jaffré, Latham and Quantin, 1971).

Recently Kelly et al (1974) have made some preliminary observations on the ecology and plant chemistry of some nickel accumulating plants from New Caledonia, most of them members of the Hybanthus family. Their work indicated a low molecular weight complex of nickel with certain amounts present as nickel (II) aqueous ions.

Out of this literature review several points emerge:

1. The toxicity and characteristic vegetation is due to the chemical composition of the parent material.
2. In accounting for surpentinic floras not only the toxic factors of serpentine soils must be considered, but also factors such as physical characteristics, soil depth, pH, calcium/magnesium ratio, magnesium, calcium, copper and other elemental concentrations.
3. In assessing the degree of toxicity other soil characteristics influencing vegetation must also be taken into consideration.

4. The possible physiological roles that nickel and chromium may have in plants which accumulate them.

This thesis reports investigations on the serpentine area known as the 'Mineral Belt' in Nelson, New Zealand and endeavours to outline a model to account for the distribution of the flora in this area. The plant chemistries of some nickel accumulating plants from New Caledonia are also investigated.

In this study the following points are considered:

(i) The chemical composition of serpentine soils and some selected plants.
(ii) Factors influencing plant distributions.
(iii) Antagonistic and mutually-stimulating plant - plant and plant-soil elemental pairs.
(iv) Statistical comparison of endemic and non-endemic plant sites.
(v) The plant chemistry of nickel.