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The nickel phytoextraction potential of some ultramafic soils as determined by sequential extraction

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Abstract

Sequential extractions at three pH values were used to model the effect of successive harvests of Ni hyperaccumulator plants on the Ni availability of several ultramafic soils. All soils, with one exception, contained about 2000 μg/g Ni and all behaved in a similar manner. It was found that between 13 and 80% of the total Ni in the soil was potentially available to plants. The remainder could not be removed even after a large number of theoretical hyperaccumulator harvests. This necessarily limits the soils' potential for phytoremediation and phytomining. The concentration of residual soluble Ni after several extractions could be predicted mathematically. As it has been shown that the Ni concentration in hyperaccumulator plants is related to the soluble Ni fraction in the soils, an estimate was made on how many economic harvests of Ni could be obtained from each soil. It was found that between three (Dun Mountain, New Zealand) and 18 (Kouaoua, New Caledonia) economic Ni extracts could be obtained before the soil would need to be modified. Similar sequential extractions may be used to determine the bioavailability of other heavy metals in soils that are to be phytoremediated or phytomined. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: nickel; phytomining; phytoremediation; sequential extraction

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1. Introduction

Commercial mining of Ni is usually performed from ores that have a high concentration of the target metal. To be economically viable, such operations require ore bodies with a relatively high (ca. 3% in New Caledonia) Ni content. Ore bodies of this nature occur only in small localised areas, and in some cases are becoming exhausted. There are however, much larger areas of low-grade ores that are not economical to exploit using current conventional methods. Most of these ore bodies are associated with ultramafic (*serpentine*) outcrops that are scattered throughout the world and usually support a characteristic flora. In serpentine-derived soils, Ni is usually present at concentrations between 0.1 and 0.7%. This is well below the minimum Ni content (3%) required for modern mining activities.

Often associated with serpentine and other metalliferous soils are plants with very unusual properties, the most notable are species that translocate large concentrations of metals to their aerial portions. These plants belong to a group known as *hyperaccumulators*, defined by Brooks et al. (1977) as plants containing a metal concentration of over 1000 μg/g (0.1%) in the above ground dry biomass. These values represent a concentration around ten times greater than the maximum metal concentration found in non-accumulator plants growing on the same substrate. At present, there are about 300 known species of hyperaccumulators of Ni.

Nicks and Chambers (1995) showed in a benchmark paper, that by growing a crop of the Ni hyperaccumulator *Strepthanthus polygaloides* on an ultramafic soil, then burning the harvested material, up to 100 kg Ni/ha could be recovered from the resulting ash (termed *bio-ore*) which had a Ni concentration of over 15%. The net economic yield of the process at that time would have been $385/ha, assuming that around 25% of the energy produced from burning could be utilised to produce electricity. This yield is similar to the net return on a crop of wheat. The process is termed *phytomining*. Since this initial study there have been two others (Robinson et al., 1997a,b) which have shown that two other species, *Alyssum bertolonii* and *Berkheya coddii* could in theory be used to extract Ni commercially from serpentine soils.

A better-known use for the above plants is a process called *phytoremediation*, which is fundamentally similar to phytomining but where the aim of the operation is to decontaminate soils polluted with heavy metals. So far the majority of phytoremediative work has focused on cadmium, lead and zinc (McGrath et al., 1993; Brown et al., 1994; Mench et al., 1994; Huang and Cunningham, 1996). However, Ni contamination is a problem in many soils associated with smelters and areas where sewage sludge has been used as a soil amendment. The above-mentioned plants may, therefore, be used to remediate such soils. Both phytoremediation and phytomining may be considered as subdivisions of the wider subject of *phytoextraction* of metals from soils.

Central to the process of phytoextraction, is the nature of the soil on which the hyperaccumulator plants are to be grown. Ernst (1996) and Robinson et al. (1997a,b) have shown that the metal concentration in the plant is proportional to the plant-available metal concentration in the soil. It was noted that a high total concentration of a given element did not necessarily indicate a high concentration of its soluble form. Predictions can be made of the expected metal concentration in plants by measuring the 'soluble' Ni content of the substrate.

In the process of phytomining, several successive crops would be grown on each site. The question then arises of how these crops would affect the bioavailability of Ni in these soils, and whether subsequent harvests would contain economically viable Ni concentrations. In the best case (for the phytominer), the available Ni in the soil will remain relatively constant in a scenario where an equilibrium situation between soluble and insoluble metal allows for full or partial replacement of the soluble fraction removed by the plant until all the metal in the soil has been removed. In a worst-case scenario, most of the metal would be matrix-bound, and once the initial metal harvest had been obtained, no further 'crops' could be grown without soil modification.

Modification may involve acidification, which was shown by Robinson et al. (1996) to increase the availability of Ni in ultramafic soils. Another possibility is the addition of chelating agents such as EDTA. However, this was found to decrease the Ni uptake of *B. coddii* despite increasing the soluble Ni (Robinson et al., 1997b). This was attributed to competition from the plant's own Ni uptake system. It is yet to be established whether this is the case for all Ni hyperaccumulators. When profitable crops can no longer be grown, the topsoil will have to be removed or ploughed to bring fresh material to the surface. If this nickel-exhausted topsoil were to be removed, however, it could still have a use as a magnesium additive to fertilisers that would contain less phytotoxic Ni than the original soil. Addition of serpentine to superphosphate fertilisers was first carried out in New Zealand during World War II when magnesium fertilisers were scarce (During, 1984). An ever-present problem with such admixtures has been the unwanted accumulation of Ni in the treated pastures.

An important factor influencing the number of Ni harvests that could be removed from a soil will be the percentage of Ni that is silicate bound or present in a very insoluble form. Such metal will never be removed by plants no matter how many crops are grown on the soil. This necessarily limits the effectiveness of any phytoextraction operation. It might be argued that, in the case of phytoremediation, the insoluble fraction of the target metal will not affect the biota and, therefore, does not need to be removed.

The aim of this study was to investigate how many theoretically economic harvests of Ni could be taken from some ultramafic soils before they would need to be modified. As it is impractical to test each soil by growing successive crops of hyperaccumulators (a process which would take many years), it was decided to use a method of sequential extractions to model the behaviour of the soil.

2. The rationale for use of sequential extraction as a model for nickel removal by successive harvests of hyperaccumulator plants

There has been much controversy about how to approximate the plant-availability of selected elements. Nevertheless, there is some agreement that chemical extraction procedures using extractants such as ammonium acetate can give some indication of this (Ernst, 1996). The aims of this study were to simulate the removal of Ni harvests from serpentine soils. Nicks and Chambers (1995) and Robinson et al. (1997a,b) have shown that to be economic, it is necessary to extract about 100 kg Ni/ha. If we assume a soil depth of 15 cm and a soil density of 1.3, removal of 100 kg of Ni from a hectare of soil (weighing ca. 2000 t) would equate to 50 μg/g Ni for a single harvest.

Studies by the above authors using the Ni hyperaccumulators *S. polygaloides*, *A. bertolonii* and *B. coddii* have shown that a single crop of a hyperaccumulator can provide 100 kg Ni/ha with the accompanying removal of 50 μg/g of the soluble Ni fraction in the soil. This is, therefore, the rationale for use of an extractant that would in theory remove this amount of Ni and hence, model the behaviour of a hyperaccumulator crop.

It has been shown (Robinson et al., 1996) that the amount of metal extracted is inversely proportional to the pH of the extractant. We have used potassium hydrogen phthalate as an extractant buffered at pH 2, 4 and 6. This extractant was chosen because the pH could be easily controlled without greatly changing the composition of the extractant. The three pH values were used to extract different amounts of Ni from the soils and were not intended to ‘model’ the pH of the rhizosphere. The most acid extract (pH 2) removed on average 85 μg/g Ni from the soils. This equates to a crop of 170 kg Ni/ha given the above conditions. The pH 4 extractant removed on average 22 μg/g Ni equating to a 44 kg Ni/ha, indicating that the 100 kg Ni/ha yield could be predicted at an extractant pH between 2 and 4. Hyperaccumulator plants extract the same

Table 1
Origin, principal minerals, nickel content (μg/g dry weight) and pH of soils used in the experiments

Country	Location	Principal minerals	Ni content	pH
New Zealand	Dun Mountain	quartz, goethite	2244	6.7
New Zealand	Rai Valley	antigorite, magnetite	2109	7.5
New Caledonia	Kouaoua	antigorite, goethite, quartz	17,208	7.2
Spain	Ojén	antigorite, quartz, olivine	1800	7.8
Spain	Puente Basadre	antigorite, quartz, talc	2100	6.3
Italy	Tuscany (Firenze)	antigorite, quartz	1609	6.9
Morocco	Taafat	antigorite, chlorite, olivine	1700	7.5

amount of Ni in a much higher pH range, presumably due to the excretion of metal-binding and metal-sequestering agents. McGrath et al. (1997) showed that rhizosphere acidification was not responsible for zinc hyperaccumulation in *Thlaspi* species. The extractants used here, removed in 24 h, the same amount of Ni as the plant would extract over a period of 1 year or more.

It must again be re-emphasised that there is no suggestion that there is any comparison between the pH values of the extractants used and the pH of the rhizosphere. The extractants are simply intended to remove similar amounts of Ni as would be extracted by hyperaccumulator plants.

3. Materials and methods

3.1. Soils studied

The soils used in these experiments and some of their properties are given in Table 1. They are comprised of minerals typically associated with serpentine soils, antigorite being common to all except for the soils from Dun Mountain, New Zealand. The concentrations of Ni are all elevated compared to ‘normal’ non-serpentine soils, which have an average Ni concentration of around 30 μg/g (Brooks, 1983). The Ni concentrations in the ultramafic soils were all well below the minimum value of 3% (30,000 μg/g) necessary for commercial mining.

3.2. Time taken for extractions to reach equilibrium

The time taken for an extraction system to reach equilibrium was of crucial importance to these experiments. Obviously, there will be a decrease in the amount of metal removed if the soil/extractant mixture has not had time to reach equilibrium. A common practice is to allow 24 h for equilibrium to be reached. To determine the time needed for Ni extractions to reach equilibrium, the following experiment was conducted on serpentine soil from the Rai Valley, South Island, New Zealand. One gram samples of soil were weighed into 20 ml centrifuge tubes and 10 ml of potassium hydrogen phthalate buffered to pH 2 was added to each. Samples were placed on an end-over-end agitator. Samples were removed after 5, 10, 15, 30, 45, 60, 135, 240, 360, 960, and 1455 min, centrifuged (3000 rpm for 5 min) and filtered. The Ni concentrations were determined by flame atomic absorption spectrometry. The results are shown in Fig. 1. The curve indicates that after 24 h, the samples were close to equilibrium. Leaving the samples for longer periods of time would increase the effect of abrasion on the soil particles, thus, giving an artificially high Ni reading. It

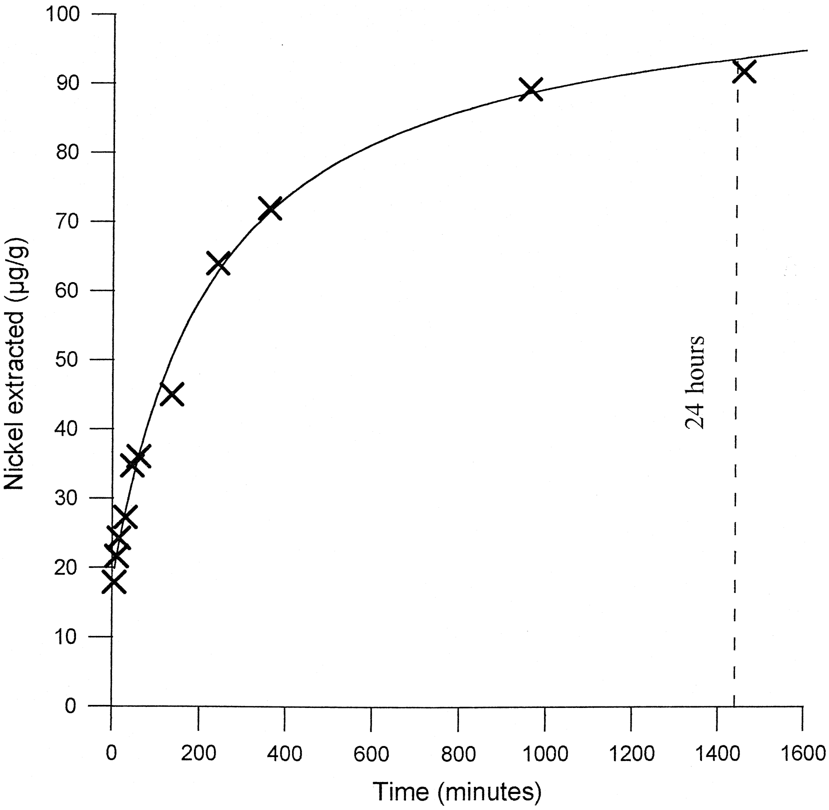

Fig. 1. Rate of extraction of nickel by potassium hydrogen phthalate at pH 2 from a New Zealand (Rai Valley) ultramafic soil.

was assumed that the time taken to reach equilibrium for the extractions at higher pH would be less, as these extractants remove less Ni.

3.3. Experimental procedure

Soils were sieved to < 0.25 mm. Three lots of 1 g of each soil were weighed accurately into 40 ml centrifuge tubes. For each soil, 10 ml of potassium hydrogen phthalate buffered with NaOH to pH values 2, 4 and 6 was added. Tubes were placed on an end-over-end agitator for 24 h. After this time period, each tube was removed, centrifuged and the top 8 ml of extractant carefully removed using an auto-pipette. This fraction was stored for analysis. Fresh extractant (8 ml) was added and the samples replaced on the agitator. This process was repeated eight times.

Extractions were also carried out with 0.1 M and 1 M HCl in an attempt to get an estimate of the potentially available (i.e., non silicate-bound) metal fraction. Solutions were analysed using flame atomic absorption spectrometry.

4. Results and discussion

4.1. Determination of the potentially available Ni fraction of the soils

Table 2 shows the concentrations of Ni extracted by using 0.1 M and 1 M HCl. The 1 M acid removed about five times the concentration of the 0.1 M extractant. This could be accounted for, if the 0.1 M extractant does not remove all the potentially available Ni, or if the 1 M acid removes some of the silicate-bound Ni. The total Ni extracted after eight extractions at pH 2 was only slightly less than that removed by the 0.1 M HCl extractant. If the rate of decrease in subsequent extractions follows the trend of the first eight, then the total Ni extracted after about 10 extractions will be greater than that extracted by 0.1 M HCl. This indicates that a stronger extractant is needed to estimate the potentially available Ni.

The cumulative quantity (average of seven different nickel-rich soils shown in Table 2) of Ni as a percentage of the total amount extracted by 1 M HCl (assumed to reflect the total non-silicate Ni) vs. the number of extractions is shown in Fig. 2. The pH 2 extractant removed the most Ni, followed by the pH 4 and 6 extractants. All three curves followed the general formula:

$$M_c = TX/(X + [T/M_1] - 1) \tag{1}$$

where M_c is the cumulative total percentage of the available metal removed, M_1 is the percentage of extractable Ni removed by the initial extract (this percentage is related to the pH and other variables such as the ionic strength of the extractant), T is the potentially available Ni percentage and X is the extraction number. Fitting curves to each of these lines gives a value of T of 39% for all three extraction curves.

Table 2
Potentially available nickel (μg/g or percentage of total) in ultramafic soils as determined by various extractants or extrapolation from Fig. 2

Location of soil	A	B	C	D
Dun Mountain (NZ)	298 (13%)	231	1040	205
Rai Valley (NZ)	925 (44%)	490	1725	373
Kouaoua (New Caledonia)	4383 (25%)	2093	6531	1760
Ojén (Spain)	1432 (80%)	483	1454	305
Puente Basadre (Spain)	432 (20%)	244	962	199
Tuscany (Firenze)	767 (48%)	286	1084	273
Taafat (Morocco)	1039 (61%)	403	1227	292

A: Calculated by extrapolation from Fig. 2.
B: Extracted with 0.1 M HCl.
C: Extracted with 1 M HCl.
D: Sum of eight cumulative extractions at pH 2.

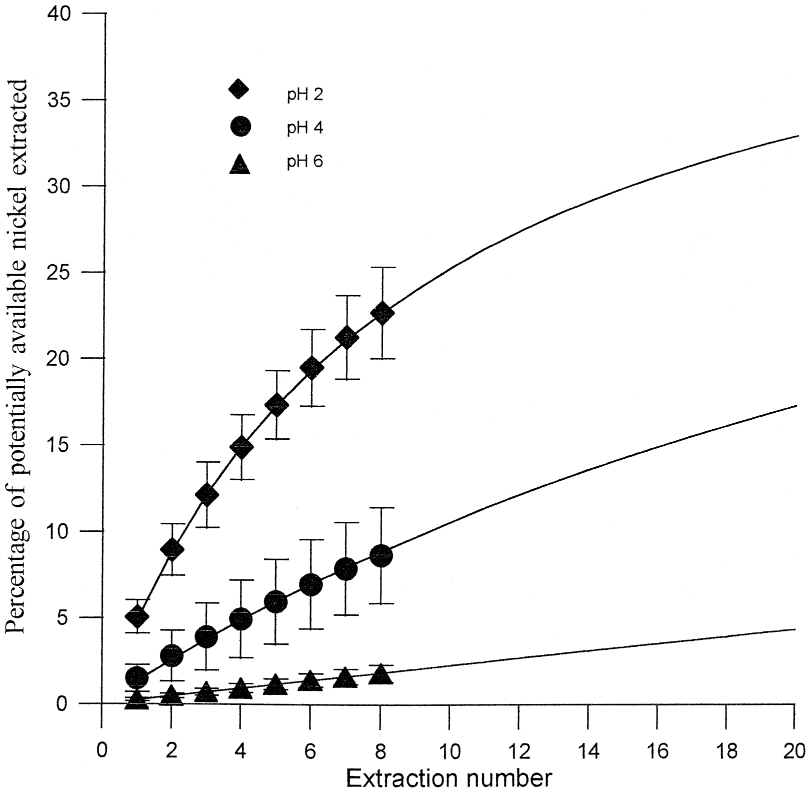

Fig. 2. The potentially available nickel content of seven different ultramafic soils as determined by sequential extractions at three pH values using potassium hydrogen phthalate.

For the seven soils tested, the calculated potentially available Ni was in the range 13–80% of the total Ni content of the soil (Table 2), showing that the total Ni concentration gives no indication of the fraction that could be removed in a phytoextraction operation. This has implications for both phytoremediation and phytomining. Heavy metals that are unavailable to plants may still be toxic if the soil itself is ingested. Wind-borne dust consumed on foodstuffs or inhaled may prove toxic if the metals are liberated in the body by stomach acids, etc. The Ni in soils that are to be phytomined needs to be available to plants as well as be present in large total concentrations.

4.2. Decrease in soluble Ni after successive harvests

Since the Ni concentration in a hyperaccumulator plant is correlated with the soluble Ni concentration in the soil (Robinson et al., 1997a), the decreasing soil Ni solubility after several harvests will affect the Ni yield of the crop. The decrease in Ni concentration of the solutions vs. extraction number is shown in Fig. 3.

Equations of the plots follow the formula:

$$M_e = T([T/M_1] - 1)/\{(X + [T/M_1] - 1)([T/M_1] - 2)\} \qquad (2)$$

where M_e is the percentage of the potential extractable metal contained in a given sequential extraction. All other symbols are as Eq. (1) above.

It must be noted that Eq. (2) is not directly dependent on pH, since it is based on M_1 the percentage of the available metal removed by the first extraction.

Although a yield of 100 kg/ha Ni has been suggested above as being economically desirable, it should be possible to have yields as low as 70 kg/ha under favourable conditions where a significant profit from incineration of biomass could be achieved. Under field conditions, the number of economic Ni harvests (> 70 kg Ni/ha and assuming an initial crop of 100 kg Ni/ha) can be calculated from Eq. (2) and the results are shown in Fig. 4. Before depletion to the limit of 70 kg/ha, the number of crops ranges from a high of about 20

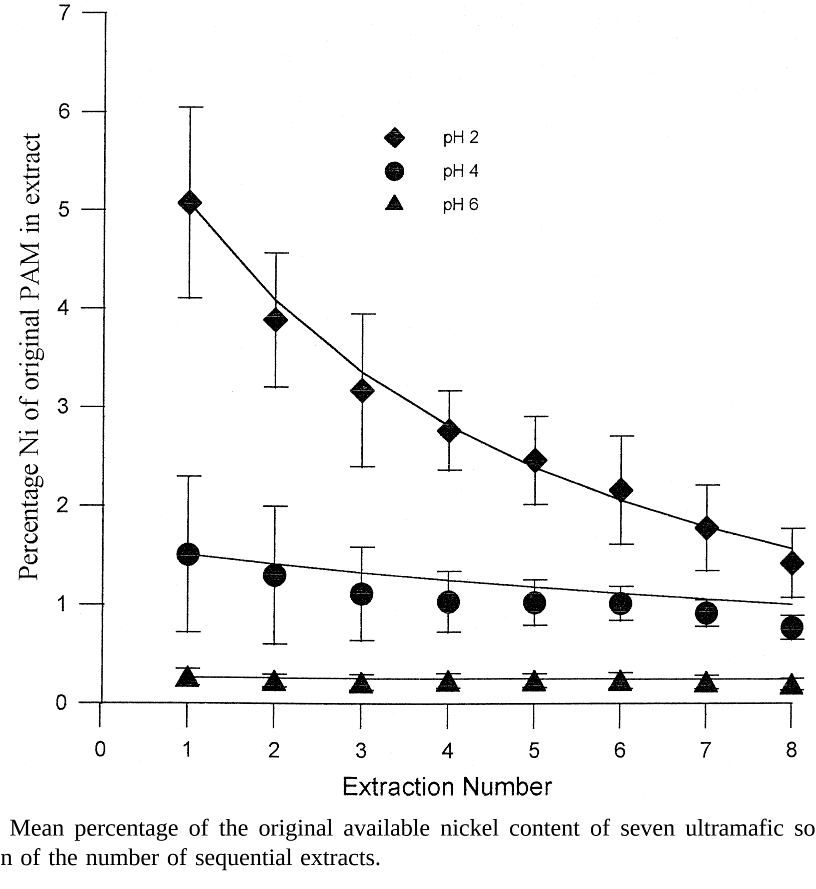

Fig. 3. Mean percentage of the original available nickel content of seven ultramafic soils as a function of the number of sequential extracts.

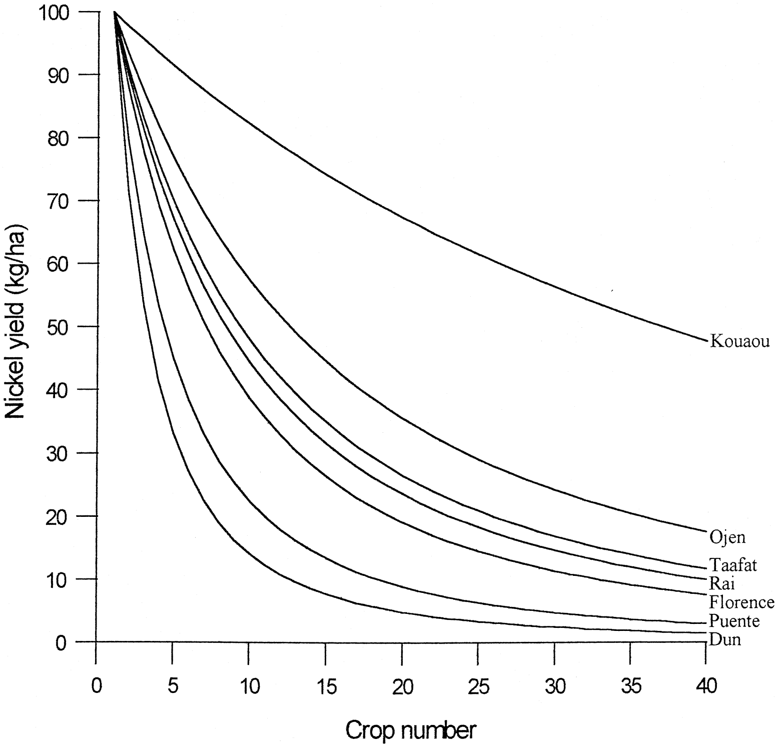

Fig. 4. Calculated nickel yields (kg Ni/ha) of successive crops of a theoretical hyperaccumulator plant growing over various ultramafic soils. The curves are based on a yield of 100 kg Ni/ha for the initial harvest that is assumed to remove 50 μg/g of the available nickel. The amounts removed, as calculated from Eq. (2), decrease with sequential extracts.

(Kouaoua) to a low of about three for Dun Mountain soils. The higher number of theoretical harvests that could be taken from the Kouaoua soil may be expected because its total Ni concentration is about an order of magnitude higher than in the other soils used in the experiments. The calculations assume a starting point of 100 kg Ni/ha and it must be remembered that Ni yields well in excess of this figure should be able to be realised. The value of 100 kg/ha is based on a soil depth of 15 cm and density of 1.3 (typical for ultramafic soils). One hectare of soil would, therefore, weigh about 2000 t and a crop with a yield of 100 kg/ha of Ni would remove 50 μg/g of the plant-available Ni in the soil. Once the lower economic limit of 70 kg/ha has been reached, ploughing to transfer subsoil to the surface should provide sufficient fresh material for more harvests.

The data in Fig. 4 show that there is a large difference between different soils in their ability to be phytomined or phytoremediated. Theoretically, the soil from Kouaoua (New Caledonia) could sustain seven times the number of theoretical harvests as the soil from Dun Mountain (New Zealand).

5. Concluding discussion

It is to be emphasised that the data in this present paper are only an approximation of the field situation. Factors such as climate, weathering, mass flow of Ni, the effect of phytometallophores, pH, Eh, presence of oxides or clays in the soil, salinity and plant or microbial variables, have not been considered here. These factors might increase or decrease the availability of Ni in soils (Stoeppler, 1992).

Despite the obvious limitations of using extractants to simulate plant behaviour, we must face the fact that time restraints preclude the use of sequential croppings in field trials over say a 20-year period to determine the plant availability of heavy metals in soils. Although chemical extractions are probably the best methods currently available to solve this problem, it is surprising that there are at present few, if any, long-term trials to assess the true correlation between simulated and actual uptake of heavy metals by plants under field conditions.

The evidence from our simulations of the ability of some soils to sustain several theoretical Ni crops indicates that phytomining could be a viable economic proposition on these soils. The sequential extraction method may also be used to investigate the behaviour of other metals such as lead, zinc and cadmium in polluted soils. These metals are contaminants of many soils near industrial sites. Many such sites are too large to be cleaned economically using conventional methods, so that phytoremediation might be the only viable decontamination method.

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