

NICKEL BIOAVAILABILITY ASSESSED BY ION EXCHANGE RESIN IN THE FIELD

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ABSTRACT

To measure nickel (Ni) bioavailability experiments were conducted in the field using ion exchange resin (IER) method. Resin bags were inserted into the upper layer of soils developed on ultramafic rocks in New Caledonia. Their Ni contents were determined after four weeks and compared to those of plant leaves of five species. Significant correlations were obtained so that the IER appeared to be successful for routine applications. Furthermore, the use of chemical reactants such as diethylenetriaminepentaacetic acid (DTPA) and KCl demonstrated to be much less reliable for assessing the bioavailability of Ni.

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INTRODUCTION

Ecosystems developed on ultramafic rocks have been widely investigated throughout the world, and their floristic, edaphic and physiological features identified (1,2,3,4,5).

In New Caledonia, outcrops of ultramafic rocks cover 5500 km², accounting for about one-third of the Grande Terre area. The chemical causes of the infertility of soils derived from ultramafic rocks are mainly due to deficiencies in major elements, such as phosphorus (P), potassium (K), and calcium (Ca). Other factors like the excess of magnesium (6) or the imbalance of the Ca/Mg ratio (1,7,8) and excessive contents of metals such as nickel (Ni) are also often pointed out, but are not evidently involved in all cases (9). Nickel affects the quantity and the quality of the crops, and its availability vary according to soil types and environments (10,11). Although the total metal content is still utilized in many countries as a quality standard of the soil, its use for the prediction of the ecological impact of metals is of little value (12). Therefore, tools to assess the bioavailability of metals to plants, especially Ni in our case, are of great interest for soil management.

The bioavailable fraction of soil metals is not only a function of the total metal content, but also is very dependent on the edaphic properties which govern the retention, transformation and mobility of toxic metals in soils (13). Various approaches have been developed to determine the bioavailable fraction of an element to plants. Many chemical reactants, including salts, diluted acids and organic ligands, have been used following different procedures, to assess the bioavailability of metals (14). Correlations between the quantities of nickel extracted from the soils by various chemical reactants and its concentrations in plants are nonetheless not always satisfactory (15). Among these reactants, L'Huillier and Edighoffer (11) demonstrated the ability of diethylenetriamine-pentaacetic acid (DTPA) to assess bioavailable Ni for various species cultivated on New Caledonian ultramafic soils. One *M* KCl also allows to examine the variability of the Ni availability in these type of soils (10).

Ion exchange resins (IER) have been used to estimate the availability of the major elements for plants (16). For trace elements, Soane and Saunder (17) were among the first to apply this method for comparing the extractability of Ni and chromium (Cr) from soils developed on Rhodesia serpentinite. They conclude that the amount of Ni extracted with a resin was closely correlated with the Ni content of the leaves of graminacea, whereas this was not the case for Cr. Hamilton and Westermann (18) show that zinc (Zn) uptake by beans is better correlated with the Zn extracted by an ion exchange resin than those extracted by DTPA. More recently, Liang and Schoenau (19) used ion exchange membranes, in greenhouse experiments, to evaluate the bioavailability of four metals [cadmium (Cd), Cr, Ni, and lead (Pb)] previously added to the soil. IER placed within a soil seemed to

adsorb effectively the metals present in the environment, and thereby simulated the action of the roots.

Thus, the aim of the present work was to test the possibility of using IER to assess the *in situ* availability of Ni in different types of soils derived from ultramafic rocks. The metal quantities adsorbed by the IER were compared with the foliar concentrations of various plant species growing naturally on these soils, and with the results obtained with two conventional reactants, 0.005 *M* DTPA and 1 *M* KCl.

MATERIALS AND METHODS

Characteristics of Soils and Flora

The study covered 6 stations representative of the main types of soils and vegetations on ultramafic rocks of the Grand Massif in the south of New Caledonia. The soils are often deep soils, primarily consisting of goethite and displaying acidic pH. Differences in the soils are essentially related to their topographic position in the landscape. Different types of soil have been distinguished: soils rejuvenated by erosion near the crests (I); highly weathered and strongly desaturated soils on the foothills (II) sometimes subject to temporary waterlogging (III); alluvio-colluvial soils on terraces subject to temporary waterlogging (IV); soils very rich in ferruginous gravels developed from the break down of ironpan with relatively high (V) or low (VI) levels of SiO₂. The soils were classified (20) as Ustic Dystropept (I), Anionic Acrudox (II, III, IV) and Anionic Acrustox (V, VI). Soil samples were collected from the upper layers (2–15 cm) after removal of litter and corresponded to the part of soil profile where the root density was the highest.

Although the vegetation of the different types of soils corresponded to different plant communities, it displayed a number of common and ubiquitous species [*Cloezia artensis* (Myrtaceae) (C); *Eriaxis rigida* (Orchidaceae) (E); *Grevillea gillivrayi* (Proteaceae) (G); *Montrouziera sphaeroidea* (Guttiferae) (M); *Scaevola beekii* (Goodeniaceae) (S)] which were selected for the foliar sampling. For each species and from each station, samples for analyses were prepared from healthy adult leaves displaying no sign of ageing, and taken from at least five different individual plants.

Chemical Analyses of Soils and Leaves

The soil samples were dried at room temperature and sieved at 2 mm before analysis. The pH was measured in a soil suspension using 1:2.5 (w/v)

soil to water ratio. Organic carbon was determined by titration using the Walkley and Black method (21). Cation exchange capacity was obtained by exchange with 1 M NH₄Cl, buffered at pH 7. Total elements were analyzed by atomic absorption spectrometry (AAS) (Varian AA300) after sample digestion by 2% HClO₄. The amounts of available metals were evaluated by AAS after extraction with 1 M KCl or 0.005 M DTPA (diethylenetriamine-pentaacetic acid) + 0.01 M CaCl₂ buffered to pH 5.3 (10). The main chemical properties of the soil samples collected from the different stations are shown in Table 1.

The leaf samples were rinsed with distilled water, dried at 80°C and powdered. Then, 2 g of powder was ashed for two hours in a muffle furnace at 450°C and the ash was solubilized in concentrated HCl. Nickel concentrations were analyzed by AAS. The Ni concentrations of the plant species selected from the different stations are given in Table 2.

IER Method

Resin bags were prepared by placing 30 cm³ of wet cation exchange resin (Dowex 50W-X4, 16–40 mesh, H⁺ form, exchangeable capacity: 250 cmol L⁻¹; Fluka), in a nylon stocking. Before use, the IER was cleaned with demonized water, placed in a syringe and eluted with 200 mL of 1 M HCl for two hours to saturate the resin with H⁺. The IER bags were stored in demonized water in a refrigerator prior to use. The bags were inserted into the 10 cm upper layers during the wet season and removed after four weeks. Four replicates of resin bags were installed in each station. After sampling, the bags were washed with demonized water to remove soil particles, placed in a syringe, and eluted with 200 ml of 1 M HCl for two hours. Preliminary test showed that more than 95% of the Ni added to the IER bags was removed by this procedure. The Ni concentrations of the eluates were determined by AAS.

Statistical Analysis

Nickel accumulated by the IER in the various stations and the Ni concentrations of the leaves of the different species were submitted to an analysis of variance (ANOVA) and their means were compared by the LSD (Least Significant Difference) test of Fisher. Relations between the foliar contents of Ni and those adsorbed on the IER were described by linear regressions and the correlation coefficients were calculated. All the calculations were done using Statistica software (StatSoft).

Table 1. Main Chemical Properties of the 2–15 cm Soil Layer of the Different Stations

Station	pH _{H2O}	Org. C (g kg ⁻¹)	CEC at pH 7 (cmol _c kg ⁻¹)	Total Elements (g kg ⁻¹)						Ni DTPA (mg kg ⁻¹)	Ni KCl (mg kg ⁻¹)
				SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MnO	NiO	NiO		
I	5.8	22.0	7.20	32.8	26.3	803.4	5.5	22.9	189	8	
II	5.1	16.2	4.57	0.9	29.9	821.3	8.5	13.1	35	4	
III	5.4	17.3	5.19	57.0	55.3	739.0	10.5	15.3	208	0	
IV	4.7	27.4	7.92	143.5	56.3	706.7	8.5	17.2	115	38	
V	5.0	9.3	3.14	228.1	43.1	556.2	2.3	4.2	2	0	
VI	4.4	17.3	6.48	0.0	34.7	820.1	1.6	3.3	2	1	

Table 2. Main Plant Species Occurrences and Ni Contents of the Leaves for the Different Stations

Stations	Species	Ni (mg kg ⁻¹)
I	<i>Cloezia artensis</i>	116
I	<i>Scaevola Beckii</i>	80
I	<i>Eriaxis rigida</i>	56
I	<i>Montrouziera sphaeroidea</i>	39
II	<i>Grevillea gillivrayi</i>	13
II	<i>Cloezia artensis</i>	132
II	<i>Scaevola Beckii</i>	80
II	<i>Eriaxis rigida</i>	90
II	<i>Montrouziera sphaeroidea</i>	24
III	<i>Grevillea gillivrayi</i>	31
III	<i>Cloezia artensis</i>	874
III	<i>Scaevola Beckii</i>	180
III	<i>Eriaxis rigida</i>	170
III	<i>Montrouziera sphaeroidea</i>	76
IV	<i>Grevillea gillivrayi</i>	29
IV	<i>Cloezia artensis</i>	1729
IV	<i>Scaevola Beckii</i>	185
IV	<i>Eriaxis rigida</i>	155
IV	<i>Montrouziera sphaeroidea</i>	111
V	<i>Grevillea gillivrayi</i>	7
V	<i>Scaevola Beckii</i>	15
V	<i>Eriaxis rigida</i>	9
V	<i>Montrouziera sphaeroidea</i>	7
VI	<i>Grevillea gillivrayi</i>	4
VI	<i>Scaevola Beckii</i>	12
VI	<i>Montrouziera sphaeroidea</i>	6

RESULTS AND DISCUSSION

Amounts of Ni Adsorbed on the IER

Nickel accumulation rates by IER varied significantly between the different stations (Table 3). The amounts of Ni that were adsorbed onto the IER ranged between 1.05 and 11.17 μM [IER bag]⁻¹. Station IV corresponding to alluvio-colluvial soil subject to temporary waterlogging was distinguished from the others by its highest content of Ni. Previous studies (10,11,22) conducted on ultramafic soils from New Caledonia, also show that the quantities of Ni extracted by KCl and DTPA, as well as the Ni content of the soil solutions, are

Table 3. Mean Contents + Standard Deviation of Ni²⁺ Adsorbed on IER for the Different Sampling Stations and Mean Concentrations \pm Standard Deviation of Ni in the Leaves for the Different Species

Stations	Ni (μM [IER bag] ⁻¹)	Species	Ni (mg kg ⁻¹)
I	4.45 \pm 2.48 ^b	C	712.8 \pm 764.2 ^b
II	5.49 \pm 0.86 ^b	E	96.0 \pm 67.4 ^a
III	6.64 \pm 1.12 ^b	G	16.8 \pm 12.5 ^a
IV	11.17 \pm 2.76 ^c	M	43.83 \pm 41.83 ^a
V	1.05 \pm 0.34 ^a	S	92.0 \pm 76.2 ^a
VI	1.80 \pm 0.31 ^a		

Comparisons of the means by the Fisher LSD test. (Element contents with the same exponent were not significantly different).

higher in waterlogged zones than in others. Nickel probably originated from the solubilization of iron oxides, which are substituted for Ni (23,24), and manganese oxide coatings, which contained easily mobilizable Ni, under redox conditions. The presence of weatherable silicate minerals related to the high level of SiO₂ (Table 1), could be also a source of available Ni (10). Then, Ni which accumulates in the organic horizons (10) could be adsorbed by IER. Stations I, II, III exhibited intermediate concentrations on the IER ranging from 4 to 7 μM [IER bag]⁻¹. Stations I and II corresponded to highly weathered soils of the crest and of the piedmont. These soils had relatively low SiO₂ contents and were probably not subject to reducing conditions. The availability of Ni was therefore limited. Despite the temporary water tables, station III that presented less manganese oxide coatings and silicate minerals exhibited lower Ni concentrations on the IER than station IV. Ni concentrations on the IER were significantly lower for gravely soils (V, VI). No difference appeared between these two stations although their large difference in SiO₂ content. The very coarse texture of these gravely soils likely reduced the contact between the soil and the resin bags, or favored the drying of the soil and hence limited the diffusion of Ni towards the IER.

Comparison of Elements Adsorbed on IER and Foliar Concentrations

The Ni concentrations of the plants (Tables 2 and 3) seemed to be specific. They were not significantly different for four species (E, G, M, S) and ranged from 17 to 92 mg kg⁻¹ (Table 3). Ni concentrations averaged 713 mg kg⁻¹ for *Cloezia artensis* (C) and reached 1729 mg kg⁻¹ in temporary waterlogged soil (station IV). According to Brooks et al. (25), this species can be considered as

hyperaccumulatrice plant for Ni as many other endemic plants of New Caledonia (3). Even if *Cloezia artensis* was recognized at first as a Ni hyperaccumulator in New Caledonia, six other species of its family (myrtaceae) have been recently determined as Ni hyperaccumulator in the serpentine flora of Cuba (26).

The Ni concentrations of the plants varied greatly with the soil type. They increased from the gravely soils to the temporary waterlogged ones as for the IER contents. The relationships between the contents on the IER and the foliar concentrations for the five plants investigated in these study are presented in Figure 1. Significant correlations (at $P = 0.1$) were found for each species but the slope of the linear regressions varied between the species.

Comparison of IER with Extractions by DTPA and KCl

In our study, the correlations between the different methods to extract Ni from the soil were generally non-significant except between IER and KCl (Table 4). The correlation coefficients between the foliar concentrations of the plants and the different extraction methods were generally lower with DTPA and KCl than those obtained with the IER (Table 4). They were only significant for *Grevillea gillivrayi* with DTPA. Uren (15) reports that the correlation factors between the Ni concentration in various plants and the Ni concentrations obtained by miscellaneous reactants are generally low. Hughes and Noble (27), who test ten reactants on soils on serpentine from east Transvaal, found that none of the reactants tested is able to predict the quantities of Ni uptake by the vegetation of these environments. L'Huillier and Edighoffer (11), nonetheless, obtained

Table 4. Correlation Coefficients Between the Quantities of Ni Extracted by the Various Reactants, and Between the Reactants and the Foliar Contents of Five Plant Species. Where n is the Number of Data Pairs (Correlation Significant at $p = 0.1$ (*), $p = 0.05$ (**), $p = 0.01$ (***))

	n	Résines	DTPA	KCl
Reactants				
DTPA	6	0.53		
KCl	6	0.83**	0.20	
Species				
C	4	0.97**	0.10	0.79
E	5	0.86*	0.58	0.44
G	5	0.86*	0.94**	0.53
M	6	0.95***	0.65	0.78
S	6	0.92***	0.74	0.59

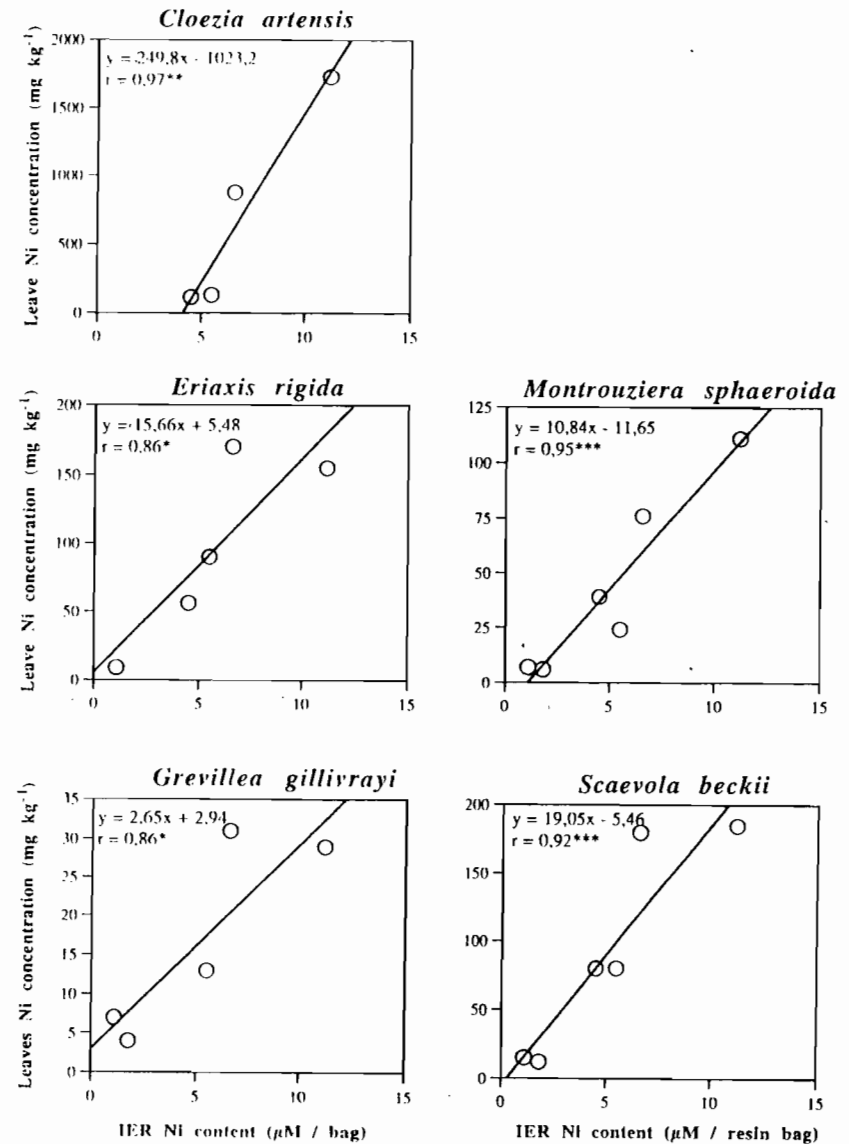


Figure 1. Relationships between quantities of Ni adsorbed to IER and foliar concentrations of the five plant species. Correlation significant at $p = 0.1$ (*), $p = 0.05$ (**), $p = 0.01$ (***)

satisfactory results with DTPA for assessing the bioavailability of Ni from New Caledonia ultramafic soils for various crops. However, Hamilton and Westermann (18), who are among the only authors who compare the resins with a chemical reactant, found that Zn extracted by resins was better correlated with the Zn concentrations of the plants than with Zn extracted by DTPA.

CONCLUSIONS

The Ni concentration of plants varied widely as a function of the plant species. The Ni hyperaccumulators are able to absorb high levels of Ni whereas the concentrations remained much lower in the others. However, good correlations between the Ni contents in the leaves and on the IER were obtained for all the species investigated. The IER demonstrated their advantage for the assessment of the bioavailability of Ni in soils over conventional reactants such as DTPA or KCl. Moreover, their use *in situ* allowed integration of the effect of various soil parameters, including the sorption of Ni on the different soil constituents (amorphous or crystallized oxides, organic matter...); the influence of soil solution composition, pH and redox conditions on the mobility and speciation of the metals. It was also a fairly simple and inexpensive method fit for routine applications. Further investigations are needed to validate the method in various pedological conditions and under different vegetations.

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