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The availability of native and applied soil cobalt to ryegrass in relation to soil cobalt and manganese status and other soil properties

Z. LI
R. G. MCLAREN*
Soil and Physical Sciences Group
P.O. Box 84
Lincoln University
Canterbury, New Zealand

A. K. METHERELL
AgResearch
c/o Soil and Physical Sciences Group
P.O. Box 84
Lincoln University
Canterbury, New Zealand

Abstract A glasshouse pot trial was conducted using 18 New Zealand grassland soils to assess the effects of soil manganese (Mn) and cobalt (Co) status, Co fertiliser and soil moisture conditions, on the plant availability of soil Co. The uptake of native and applied Co by ryegrass was measured, and attempts made to determine the main factors influencing plant Co concentrations. There were highly significant relationships between ryegrass Co concentrations and total soil Mn, and EDTA-extractable and $CaCl_2$-extractable soil Mn; ryegrass Co concentrations decreasing in a curvilinear fashion with increasing soil Mn levels. Similar relationships were observed between ryegrass Co concentrations and Mn determined in individual soil fractions as determined using a sequential fractionation technique. It was therefore clearly demonstrated that soil Mn status plays a crucial role for soil Co availability. Soils with high Mn contents have a high probability of strong fixation of soil Co and showed negligible responses to Co fertiliser treatment. For the soils in this study, which had a large variation in Mn status, soil Co extractants were poor predictors of Co availability to plants. However, soil Co fractionation data suggests that Co in the organic-bound fraction is probably one of the important sources of supplying Co in soils for plant uptake.

Keywords cobalt; manganese; ryegrass; soil moisture

INTRODUCTION

For the past few decades, in New Zealand as well as in other countries dominated by pastoral agriculture, substantial efforts have been put towards ensuring adequate pasture cobalt (Co) levels and thus preventing Vitamin B_{12} deficiencies in grazing ruminants (McLaren et al. 1987; Metherell 1989; Sherrell 1990; Sherrell et al. 1990). Many New Zealand soils are known to be potentially Co-deficient (Andrews 1970; O'Connor et al. 1995; Li et al. 2001a). However, as a result of extremely low Co concentrations, strong fixation by soil, and sensitivity to changes in soil properties such as pH and water potential (Adams et al. 1969; McLaren et al. 1985; Metherell 1989), the evaluation of soil Co status in relation to plant availability is complex. In particular, because of the ability of soil manganese (Mn) oxides to scavenge trace elements, Co availability in soil is strongly affected by soil Mn status (Adams et al. 1969; Tiller et al. 1969; Childs 1975).

A recent investigation of Co and Mn in permanent grassland soils from four different regions of New Zealand (Li et al. 2001a) confirmed a strong association between these two elements. A more detailed study (Li et al. 2001b) used a sequential fractionation technique to determine the forms and concentrations of Co and Mn in 18 New Zealand grassland topsoil samples. The conclusions from this study (Li et al. 2001b) were that, although soil Mn may not have a substantial effect on the overall distribution of Co in soils, the Co associated with the Mn oxide fraction might significantly affect the plant availability of soil Co.

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*Author for correspondence.

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The objectives of the present study, with the same 18 soils used in the fractionation study, were to conduct a glasshouse experiment to assess the effects of soil Mn status, Co fertiliser, and soil moisture conditions, on the availability of soil Co. Ryegrass was selected as the test plant since it is a dominant species in many improved New Zealand pastures. Although the results of pot trials in glasshouse conditions may not be directly applicable to the field situation, the strict control of soil and plant growth conditions increases the possibility of assessing which soil factors influence plant uptake of trace elements. In a study on soil Co uptake by plants the moisture status of the soil must be controlled, and this is done more easily under glasshouse conditions. Pot trials also remove the risk of soil contamination during herbage sampling.

MATERIAL AND METHODS

Soils and soil characterisation

Eighteen topsoil samples (0–10 cm) from grassland sites throughout New Zealand were used for the pot trial. These same soils were also used in the previous fractionation study (Li et al. 2001b), and some relevant chemical and physical properties of the experimental soils are listed in Table 1. Soils were selected to provide a wide range in Co and Mn levels. All soil samples were air-dried and ground to pass through a 2-mm stainless steel sieve prior to laboratory analysis. Soil pH was measured in a water suspension using a soil:solution ratio of 1:2.5. Organic carbon (C) contents in the soils were determined by LECO CNS 2000 analyser, and soil texture (clay content) using a Malvern Mastersizer laser particle sizer. Total Co and Mn were determined using a nitric acid microwave digestion method (USEPA SW 846-3015). EDTA-extractable Co and Mn were determined by extraction with 0.02 *M* Na_2H_2EDTA (pH 7.0) for 16 h on an end-over end shaker (5 g soil, 20 ml extractant) (Li et al. 2001a). Calcium chloride-extractable Co and Mn were determined by extraction with 0.05 *M* $CaCl_2$ for 24 h on an end-over end shaker (4 g soil, 20 ml extractant). Both types of extract were centrifuged at 10 000 rpm for 10 min before filtering through a Whatman No. 42 filter paper.

Bulk soils for the pot experiment were maintained in field-moist condition and were passed through a 6-mm sieve to remove pasture roots and gravel prior to their use. Soil moisture contents were determined by the oven drying gravimetric method. The moisture contents of the individual soils at field capacity (FC) were obtained using a moisture tension table (– 1000 mm H_2O). The soil packing densities varied from 0.6 to 1.2 g cm^{-3} depending on the physical properties of the individual soils.

Pot experiment

The treatments of the pot experiment are summarised in Table 2. The treatments with or without added Co were laid out as separate concurrent sub-experiments. Due to lack of sufficient soil samples, only 15 of the soils were used for the added Co series. Set amounts of each of the soils were weighed into 1-litre plastic pots according to the packing densities of the individual samples as used in the determination of FC moisture contents. Co fertiliser, where appropriate, was applied to soils in deionised water solution so that each pot received 350 μg $CoSO_4 \cdot 7H_2O$. This was approximately equivalent to the addition of a general Co application of 350 g $CoSO_4 \cdot 7H_2O$ ha^{-1} in New Zealand (the applied Co is assumed to be retained in the top 0–10 cm layer of soil).

In each of three replicate pots, approximately 20 ryegrass seeds were sown. The soils were then watered daily and the tops of the pots were covered with polythene sheeting and shaded from sunlight until germination of the seed had taken place. The soils were then adjusted to two moisture levels by weight: field capacity and 70% FC, and the pots were arranged in a completely random design in the glasshouse. The pots and soils were weighed three times a week and the required weight of deionised water was added to maintain the soils at the specific moisture levels. Approximately 60 days after seed germination, the herbage from the pots was harvested at 1 cm above the soil surface, using stainless steel scissors, dried at 80°C and weighed. Plant material (1 g), finely ground using a stainless steel roller, was digested in a mixture of concentrated HNO_3, $HClO_4$, and H_2SO_4 (10 ml; 40:4:1), and Co concentrations in the digests determined as described below.

Elemental analysis

Manganese concentrations in soil extracts and digests were determined directly by flame atomic absorption spectrophotometry (FAAS). Cobalt concentrations in EDTA extracts and nitric acid digests were determined directly by graphite furnace atomic absorption spectrophotometry (GFAAS). Cobalt in $CaCl_2$ extracts and in plant digests was

Table 1 Properties of the soils used for the pot experiment.

Soil	New Zealand classification[1]	pH	Org. C	Clay	Total Fe	Total Co	Total Mn	EDTA-Co	EDTA-Mn	$CaCl_2$-Co	$CaCl_2$-Mn
			%	%	%	$\mu g\ g^{-1}$					
Tutira	Pumice Soil	5.30	6.99	6.0	0.41	0.44	50	0.04	16.5	0.020	6.3
Matawai	Pumice Soil	5.01	4.97	7.6	0.50	1.82	229	0.50	73.8	0.051	11.3
Gisborne 1	Pumice Soil	5.14	9.54	10.2	0.27	2.23	584	1.08	324	0.048	50.8
Akatore	Brown Soil	5.19	10.23	7.9	3.22	2.93	121	0.03	8.9	0.015	3.5
Taieri	Gley Soil	5.38	2.75	24.6	2.22	3.44	216	0.35	30	0.049	9.7
Gisborne 2	Pumice/Brown	5.30	6.06	14.1	0.90	4.31	648	1.63	366	0.058	59.8
Naike 1	Granular Soil	4.39	15.34	9.7	2.52	5.11	225	0.10	17.7	0.090	28.1
Waimakariri	Recent Soil	5.61	2.37	14.5	2.08	6.09	301	1.03	35.4	0.079	5.9
Lismore	Brown Soil	5.36	3.56	18.5	2.39	6.24	366	1.26	91.0	0.071	16.8
Mangaotaki	Allophanic Soil	4.92	5.53	25.0	2.44	6.37	697	2.11	401	0.132	98.0
Selwyn	Recent Soil	5.45	2.84	16.9	1.78	7.11	339	1.01	29.5	0.060	5.5
Mangapiko	Recent Soil	4.97	9.81	10.0	3.04	7.57	965	1.29	268	0.061	52.1
Tuturau	Brown Soil	5.80	5.62	14.9	2.92	7.70	390	0.85	85	0.014	14.6
McNab	Brown Soil	5.12	4.40	16.1	2.57	9.24	893	2.49	231	0.055	21.9
Matapiro	Pallic Soil	5.48	3.41	19.1	1.45	10.70	1512	6.45	964	0.023	51.3
Kauroa	Allophanic Soil	5.28	8.88	8.7	4.51	11.28	3186	2.61	972	0.100	76.2
Makarewa	Gley Soil	4.95	6.18	9.8	4.08	14.00	1030	1.30	193	0.061	31.5
Naike 2	Granular Soil	5.24	5.82	26.9	4.28	14.66	4592	4.58	1874	0.015	75.3

[1] Hewitt (1993).

determined by GFAAS, following a solvent extraction procedure involving complexation as the Co-nitroso-R-complex and separation into 4-methyl pentan-2-one (MIBK) (Mountjoy 1970).

RESULTS AND DISCUSSION

Although there was some variation in the weight of plant dry matter harvested from different soils and moisture treatments, this appeared to have little effect on the concentration of Co measured in the ryegrass. The ryegrass Co concentrations from neither native nor applied Co were significantly correlated with dry matter yield.

Effect of soil moisture on ryegrass Co concentration

Ryegrass Co concentrations are shown in Table 3. Overall, there was no significant difference in ryegrass Co concentration between the two moisture levels for soils without added Co. For soils with added Co, there was a significant difference in ryegrass Co concentration between the two moisture conditions, with a lower mean Co concentration at the higher moisture treatment (Table 3). For the soils both with and without added Co there was a significant soil by moisture treatment effect. However, the overall effect of moisture was very small and there was no consistent pattern between soils. For some individual soils, Co concentrations were highest at the lower moisture level, and for others the reverse was true. The effect of soil moisture conditions on plant Co concentration has been reported by many researchers. It has been noted that poor drainage status may increase the uptake of Co and other trace elements, a phenomenon attributed to the reduction and dissolution of Mn and Fe oxides, and release of associated trace elements (Hill et al. 1953; Mitchell et al. 1957; Adams & Honeysett 1964; Berrow et al. 1983). Under field conditions, Metherell (1989) reported that seasonal fluctuations in herbage Co concentration were closely associated with the soil moisture conditions, and the lowest Co levels were observed in the driest months. However, in the present pot trial, the lack of a consistent effect of soil moisture conditions on the ryegrass Co concentrations for soils with and without added Co might be due to a combination of factors.

For many soils, plant yields were substantially higher in pots maintained at 100% FC than in those maintained at 70% FC. This was most probably related to the relatively small amounts of soil in each pot, and high moisture evaporation rates caused by relatively high temperatures in the glasshouse during this experiment. Under such conditions, it appears that the watering regime, three times a week, did not maintain the soil moisture conditions at the designated levels. Thus it is highly unlikely that soil moisture conditions were ever wet enough to cause the increases in Co availability observed by previous researchers. However, the increases in plant yield achieved by increasing soil moisture from 70 to 100% FC did result in corresponding increases in total Co uptake. There was indeed a very strong (almost 1:1) correlation between % increased Co uptake and % yield increase as the moisture content increased from 70 to 100% field capacity (Fig. 1). This explains the lack of moisture effect on plant Co concentrations as described above (i.e., the increase in growth and corresponding increase in Co uptake with increased moisture kept the Co concentration constant).

Table 2 Pot experiment treatments.

No. of soils	Co treatment	Soil moisture level
18	Zero	Field capacity
18	Zero	70% Field capacity
15	350 µg $CoSO_4.7H_2O$/pot	Field capacity
15	350 µg $CoSO_4.7H_2O$/pot	70% Field capacity

As a result of the lack of difference between moisture treatments on plant Co concentrations, to simplify discussions in the following sections, results have been averaged across the two moisture treatments.

Table 3 Co concentrations in ryegrass grown in soils with and without added Co. FC, field capacity.

	Ryegrass Co (no added Co) µg g^{-1}			Ryegrass Co (added Co) µg g^{-1}		
Soil	70% FC	100% FC	Mean	70% FC	100% FC	Mean
Tutira	0.097	0.080	0.089	0.282	0.170	0.226
Matawai	0.057	0.087	0.072	0.123	0.155	0.139
Gisborne 1	0.028	0.029	0.029	–	–	–
Akatore	0.084	0.112	0.098	0.171	0.172	0.172
Taieri	0.070	0.073	0.072	0.153	0.199	0.172
Gisborne 2	0.019	0.029	0.024	–	–	–
Naike 1	0.049	0.042	0.046	0.080	0.091	0.086
Waimakariri	0.088	0.065	0.077	0.198	0.104	0.151
Lismore	0.038	0.028	0.033	0.048	0.043	0.046
Mangaotaki	0.029	0.024	0.027	0.048	0.036	0.042
Selwyn	0.055	0.052	0.054	0.090	0.070	0.080
Mangapiko	0.026	0.025	0.026	0.040	0.036	0.038
Tuturau	0.019	0.026	0.023	0.050	0.047	0.049
McNab	0.032	0.024	0.028	0.045	0.040	0.043
Matapiro	0.023	0.030	0.027	–	–	–
Kauroa	0.033	0.042	0.038	0.031	0.040	0.036
Makarewa	0.023	0.019	0.021	0.020	0.019	0.020
Naike 2	0.014	0.027	0.021	0.021	0.028	0.025
Mean	0.043	0.045	0.044	0.093	0.083	0.088

	$LSD_{5\%}$ (no added Co)	$LSD_{5\%}$ (added Co)
Soil/moisture interaction	0.017	0.009
Moisture treatments	not significant	0.004
Soil differences	0.006	0.017

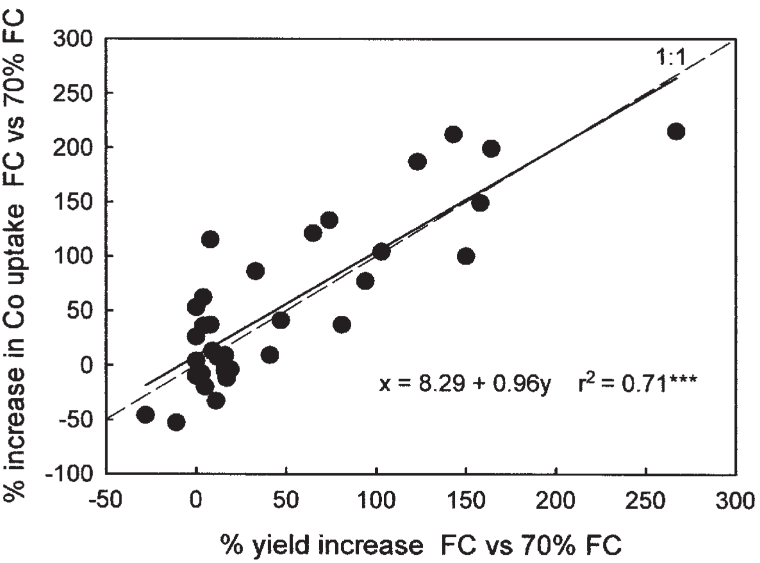

Fig. 1 Relationship between proportional increases in ryegrass Co uptake and plant yield brought about by increasing soil moisture status from 70% field capacity to 100% field capacity.

Ryegrass Co concentrations in relation to extractable soil Co and Mn

Simple correlation coefficients for the linear relationships between the concentrations of ryegrass Co and the concentrations of total and extractable soil Co and Mn are presented in Table 4. $CaCl_2$-extractable Co is considered to be a measure of soluble and exchangeable soil Co, the most bioavailable forms of Co. However, there were no significant correlations between ryegrass Co concentrations and soil $CaCl_2$-extractable Co in the present pot trial. This conclusion is in direct contrast to an earlier observation, in a pot trial of 20 soils from south-east Scotland, that pasture Co concentration was significantly correlated with soil $CaCl_2$-extractable Co (McLaren et al. 1987). However, in the study by McLaren et al. (1987), the range of $CaCl_2$-extractable Co concentrations (0.001–0.485 $\mu g\ g^{-1}$) was much wider, and the range in total Mn concentrations (140–572 $\mu g\ g^{-1}$) much narrower, than in the present study (see Table 1). Soluble and exchangeable Co concentrations, as assessed by $CaCl_2$ extraction of field-moist soil, are extremely low (Li et al. 2001a), and much larger proportions of soil Co are associated with soil Mn and Fe oxides (Li et al. 2001b). It is possible that plant roots absorb Co by localised dissolution of amorphous Mn and Fe oxides resulting from a region of low pH around the root surface and the presence of root exudates. Thus, Co that is specifically sorbed by the oxides could be released and absorbed by the root. Indeed, the "contact absorption" of Mn ions from apparently insoluble Mn oxides by plant roots has been reported elsewhere (Leeper 1934; Bromfield 1958, 1959) and was discussed extensively by Uren et al. (1988). In the presence of such a mechanism, the relative importance of soluble and exchangeable Co may be quite low.

Total or EDTA-extractable Co could be considered to measure solid phase forms of Co that can be potentially solubilised in the root environment. Somewhat surprisingly at first glance, in the present pot trial ryegrass Co was significantly negatively correlated with both total soil and EDTA-extractable Co (Table 4). However, ryegrass Co concentrations were also significantly negatively correlated to total and EDTA-extractable Mn (and

Table 4 Correlation coefficients (*r*) for the linear relationships between ryegrass Co concentrations and soil properties. *, $P < 0.05$; **, $P < 0.01$; ***, $P < 0.001$.

	Ryegrass Co	
Property	no added Co	added Co
$CaCl_2$-Co	–0.20	–0.19
$CaCl_2$-Mn	–0.66**	–0.62*
EDTA-Co	–0.54*	–0.67**
EDTA-Mn	–0.47*	–0.48
Total Co	–0.64**	–0.83***
Total Mn	–0.45	–0.52*
Total Fe	–0.29	–0.67**
Total organic C	–0.01	–0.06
Soil pH	0.09	0.17
Clay content	0.35*	0.30

to $CaCl_2$-extractable Mn). There is known to be a significant positive relationship between Co and Mn, extracted by either nitric acid (total) or EDTA extraction, in New Zealand soils (Li et al. 2001a). The above correlations suggest that soil Co availability is influenced more by soil Mn status than the actual concentration of Co present in the soil. Certainly, the results provide more evidence that techniques such as acid digestion and/or relatively strong extraction with EDTA, on their own are inadequate in assessing the concentration of plant available Co for soils with wide ranges in Mn status. McLaren et al. (1987) also noted, in their pot trial on 20 soils from south-east Scotland, that there was no significant correlation between pasture Co concentration and soil EDTA-extractable Co. In contrast, however, Mitchell et al. (1957) reported a highly positive significant correlation between the Co contents of mixed herbage, ryegrass, and clover and the concentrations of soil Co extracted by EDTA. In addition, Lakanen & Ervio (1971) suggested that acid ammonium acetate/0.02*M* EDTA was a suitable soil extractant for trace metals, and EDTA-extractable Co had also been successfully used to evaluate the pasture Co status and Co fertiliser accumulation effect on pumice soils in New Zealand (Forbes 1976; Sherrell et al. 1980, 1990; Sherrell 1990). These conflicting observations may be due, to a certain extent, to the different soil Mn status of the soils used in these studies. Unfortunately, however, apart from the study by McLaren et al. (1987), none of the above papers reported soil Mn concentrations. On soils of similar geological origin and development, particularly young soils, there may be good opportunities to observe some relationship between pasture Co concentration and soil EDTA-extractable Co.

As noted above, in the present pot trial, ryegrass Co concentrations, both with and without added Co, were negatively correlated with the total, EDTA-extractable and $CaCl_2$-extractable Mn (Table 4). However, graphical examination of the data suggested that the relationships between ryegrass Co concentrations and soil extractable Mn concentrations were in fact curvilinear. Indeed the relationships were much improved by fitting the data to a simple two-parameter power function model:

$$y = ax^b \qquad (1)$$

where y = plant Co concentration, x = soil Mn concentration and a and b are constants. The resulting equations and correlation coefficients are shown in Table 5.

The fitted curvilinear relationships between plant Co concentrations and total soil Mn for both the soils with and without added Co are shown in Fig. 2. The relationships with EDTA-extractable and $CaCl_2$-extractable Mn were similar, and demonstrate clearly the important effect of soil Mn on plant Co concentration. The difference between the fitted curves in Fig. 2 suggest that responses to added Co concentration are highest at low soil Mn concentrations and decrease rapidly as soil Mn concentrations increase. This is demonstrated more clearly by the data in Fig. 3 in which the increases in plant Co concentration are plotted against total soil Mn. The data indicates that for soils with total Mn concentrations above 1000 mg kg^{-1}, there is likely to be little response in plant Co concentration to additions of Co to the soil. It is interesting to note

Table 5 Curvilinear relationships between ryegrass Co concentrations (μg g^{-1}) and soil Mn concentrations (mg kg^{-1}). *, $P < 0.05$; **, $P < 0.01$; ***, $P < 0.001$.

Relationships for soils without added Co	
Plant Co = $0.172(CaCl_2\text{-}Mn^{-0.474})$	$r = 0.86$***
Plant Co = $0.188(EDTA\text{-}Mn^{-0.324})$	$r = 0.84$***
Plant Co = $0.509(Total\ Mn^{-0.405})$	$r = 0.82$***
Relationships for soils with added Co	
Plant Co = $0.391(CaCl_2\text{-}Mn^{-0.560})$	$r = 0.78$***
Plant Co = $0.487(EDTA\text{-}Mn^{-0.412})$	$r = 0.80$***
Plant Co = $2.018(Total\ Mn^{-0.537})$	$r = 0.89$***
Relationships for increase in plant Co resulting from added Co	
Increase in plant Co = $0.214(CaCl_2\text{-}Mn^{-0.628})$	$r = 0.69$**
Increase in plant Co = $0.297(EDTA\text{-}Mn^{-0.484})$	$r = 0.73$**
Increase in plant Co = $2.056(Total\ Mn^{-0.682})$	$r = 0.86$***

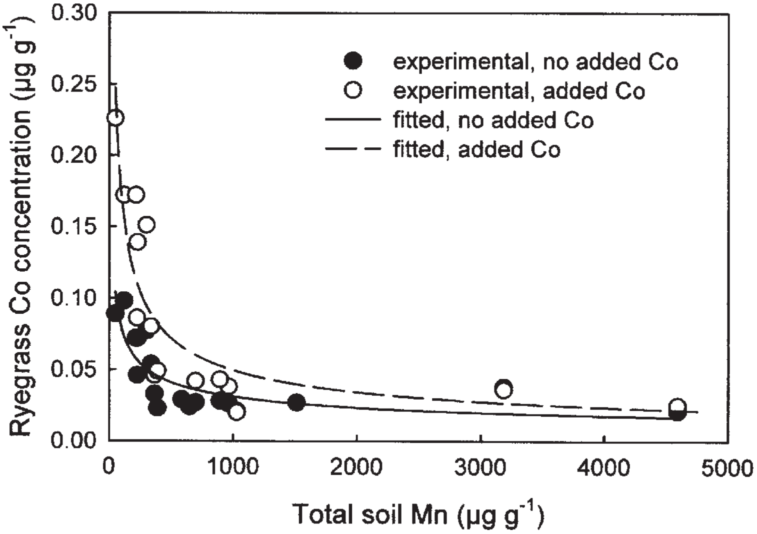

Fig. 2 Effect of total soil Mn on ryegrass Co concentration (fitted lines from curvilinear relationships, Table 5).

that a similar conclusion was reached by Adams et al. (1969) in their study of some Australian soils. The corresponding Co response limit for EDTA-extractable Mn was approximately 500 mg kg^{-1} and for $CaCl_2$-extractable Mn, approximately 30 mg kg^{-1}.

In the case of the soils with added Co, in addition to the relationship with soil Mn, there was also a significant linear relationship between plant Co concentration and total soil Fe (Table 4). However, unlike for Mn, the data points did not show a strong curvilinear relationship and indeed were quite widely scattered. Thus, in this study, Fe did not appear to have a marked effect on plant Co concentrations.

Ryegrass Co in relation to Co and Mn in individual soil fractions

In an attempt to obtain additional information on the relationships between plant Co concentrations and soil Co, Mn, and Fe, correlations were examined between ryegrass Co concentrations and the concentrations of Co, Mn, and Fe in individual soil fractions, as determined by sequential fractionation (Table 6). The fractionation data used for the correlations have been published previously by Li et al. (2001b).

The linear correlations produced similar results to those obtained with the single extractions already discussed. Ryegrass Co concentrations, both with and without added Co, were negatively correlated to the Mn concentrations in the exchangeable, amorphous Fe-oxide and crystalline Fe-oxide fractions, and to the Co content in amorphous Fe-oxide, crystalline Fe-oxide and residual fractions (Table 6). In the case of ryegrass Co concentrations without added Co, significant negative correlations were also obtained with Fe in the crystalline Fe oxide and residual fractions. As with the single extract data, correlations involving Mn were substantially improved using the curvilinear relationship shown in Equation 1 (Table 6). This was not the case for correlations involving Co and Fe, where correlations were not improved, or only marginally so, by using the curvilinear relationship. The curvilinear relationships with Mn were very similar to those shown in Fig. 2, with very little scatter around the curves. In contrast, data for Fe and Co showed considerable scatter, with little in the way of clear trends. The correlations between ryegrass Co concentrations and with Mn in the various fractions were clearly the dominant relationships observed.

The apparent importance of the soil oxide fractions is no doubt due to the ability of Fe and/or Mn oxides to strongly sorb Co (e.g., McKenzie 1967; Forbes et al. 1976; Bibak 1994), thus decreasing solution Co concentrations and reducing plant bioavailability. Cobalt is known to be specifically sorbed on the surface of Mn and Fe oxides by exchanging with bound H^+, and by exchange with Mn^{2+} and Mn^{3+} in the crystal lattice of Mn oxides (McKenzie 1970; Loganathan & Burau 1973).

One problem recognised with fractionation data is that if total element concentrations vary widely between the experimental soils, the relative importance of individual fractions may be obscured.

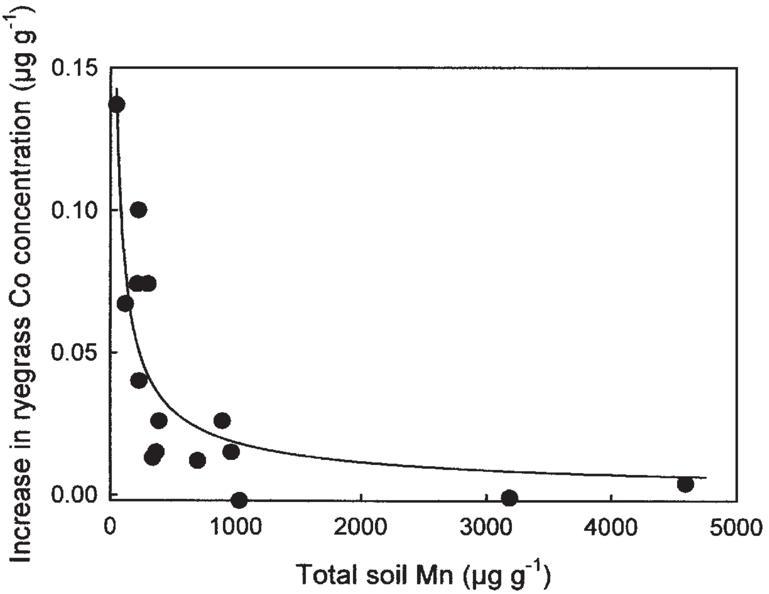

Fig. 3 Effect of total soil Mn on plant Co concentration response to added soil Co (line fitted from curvilinear relationship, Table 5).

To overcome this, concentrations of elements in individual fractions can be "normalised" by calculating ratios to the total element concentrations. In the present study, ratios of Co and Mn in individual fractions to total Co and Mn have been calculated and correlated with ryegrass Co concentrations (Table 7).

Relatively strong positive correlations were obtained between ryegrass Co concentrations, both with and without added Co, and the ratios of organic-

Table 6 Correlation coefficients (*r*) for the relationships between ryegrass Co concentrations and Co, Mn, and Fe in individual soil fractions. *, $P < 0.05$; **, $P < 0.01$; *** $P < 0.001$.

	Ryegrass Co (no added Co)		Ryegrass Co (added Co)	
Fraction	linear	curvilinear[1]	linear	curvilinear[1]
Exchangeable Co	–0.18		–0.18	
Exchangeable Mn	–0.62**	0.82***	–0.56*	0.72**
Organic-bound Co	0.09		0.11	
Organic-bound Mn	–0.35		–0.35	
Mn oxide-bound Co	–0.38		–0.56	
Mn oxide-bound Mn	–0.34		–0.37	
Amorphous Fe oxide-bound Co	–0.62**	0.75***	–0.77***	0.86***
Amorphous Fe oxide-bound Mn	–0.56*	0.87***	–0.63*	0.90***
Amorphous oxide Fe	0.14		–0.20	
Crystalline Fe oxide-bound Co	–0.63**	0.64**	–0.78***	0.82**
Crystalline Fe oxide-bound Mn	–0.53*	0.78***	–0.63*	0.87***
Crystalline oxide Fe	–0.37		–0.66**	0.67**
Residual Co	–0.47*	0.44	–0.72**	0.70**
Residual Mn	–0.30	0.52*	–0.45	0.77***
Residual Fe	–0.33		–0.64*	0.65**

[1] Using Equation 1.

bound Co and Mn to total Co and Mn. This suggests that Co associated with soil organic matter is probably an important source of Co for plant uptake. Although the proportions of Co in the soil organic matter fraction are relatively small for most soils (mean 0.068 for soils in this study), the absolute concentrations are far in excess of plant requirements. The relationship between ryegrass Co and organic-bound Mn is most likely due to a very strong correlation between the proportions of total soil Co and Mn in the organic-bound fraction (r = 0.93***). This correlation is yet further evidence of the strong association between Co and Mn in soils. It is hypothesised that since soil organic matter, as a major source of electrons, is intimately involved in the reduction of soil Mn oxides, release of Mn and associated Co by this process is likely to result in accumulation at organic binding sites. Apart from the correlations with organic-bound Co and Mn, there were also some significant correlations with the proportions of total Mn and Fe in the amorphous oxide fraction, again stressing the importance of this fraction for the plant availability of soil cobalt.

Ryegrass Co concentrations in relation to soil pH

Relationships between plant Co concentrations and soil pH have been frequently observed in the past (e.g., Reith & Mitchell 1960; Adams et al. 1969; Graham 1973). However, in the present study, over all 18 experimental soils, there was no significant correlation between soil pH and ryegrass Co concentrations for soils either with or without added Co (Table 4).

A negative relationship between plant Co concentration and soil pH has been demonstrated previously both in field and glasshouse pot experiments (Beeson et al. 1948; Wright & Lawton 1954; Reith & Mitchell 1960; Mokragnatz & Filipovic 1961; Singh & Singh 1966; Graham 1973). Adams et al. (1969), in their pot trial, observed that decreasing soil pH increased uptake of both native and applied Co by clover. McLaren et al. (1987), also in a glasshouse pot trial, obtained a close negative association between soil pH and plant Co concentration. However, in the present study the large dependence of Co concentration on soil Mn (see above), and the limited range of pH in the soils studied (4.4–5.8 with only one soil lower than pH 4.9), may well have obscured any effect of soil pH. It should be noted that the total Mn contents of the 20 experimental soils in the study by McLaren et al. (1987) ranged from 140 to 575 $\mu g\ g^{-1}$, a much smaller range than that of the soils used in the present pot trial (50–4592 μg Mn g^{-1}).

However, as in the present study, Nicholls & Honeysett (1964) and Reddy & Mehta (1961) obtained no relationship between soil pH and the plant assimilation of soil Co. It is difficult to compare the results from those studies with that of the present pot trial because there were no soil Mn contents

Table 7 Linear correlation coefficients (r) for the relationships between ryegrass Co concentrations and the ratios of Co, Mn, and Fe in individual soil fractions to total soil Co, Mn or Fe. *, $P < 0.05$; **, $P < 0.01$; *** $P < 0.001$.

Co/Mn/Fe in fraction (Total soil Co/Mn/Fe)	Ryegrass Co no added Co	 added Co
Exchangeable Co	0.44	0.69*
Exchangeable Mn	0.01	0.21
Organic-bound Co	0.57*	0.76***
Organic-bound Mn	0.51*	0.65**
Mn oxide-bound Co	–0.01	0.42
Mn oxide-bound Mn	–0.45	–0.34
Amorphous Fe oxide-bound Co	–0.10	–0.08
Amorphous Fe-oxide-bound Mn	–0.65**	–0.60*
Amorphous oxide Fe	0.44	0.75***
Crystalline Fe oxide-bound Co	0.04	0.13
Crystalline Fe oxide-bound Mn	0.36	0.34
Crystalline oxide Fe	–0.40	–0.346
Residual Co	0.19	–0.02
Residual Mn	0.52*	0.35
Residual Fe	–0.30	–0.47

reported. However, the soil types used by Nicholls & Honeysett (1964) were similar to those used in the study by Tiller et al. (1969) that ranged in Mn concentration from 18 to 12 600 μg g^{-1}. On this assumption, it is not surprising that soil pH showed little effect on pasture Co concentrations with such a wide range in soil Mn status.

From the data of the present pot trial and comparisons with other studies, it is concluded that the presence or absence of an effect of soil pH on Co availability is probably due mainly to the Mn status in soils used in the reported studies. In trials using soils with a considerable variation of Mn contents, the effect of soil pH on pasture Co concentration might be masked by the strong fixation of Co by soil Mn minerals. However, in trials with relatively low contents and/or narrow ranges of soil Mn, the pH effect might be more dominant.

In the present study, in addition to the single correlations reported in the above sections, detailed multiple regression analyses were also carried out in an attempt to extend the data interpretation. However, in general, the effects of Mn on plant Co concentrations appeared to be so dominant that the incorporation of other soil properties, such as soil pH, into regressions did not improve their significance.

CONCLUSIONS

The results from this study clearly demonstrate that soil Mn status plays a crucial role in plant uptake for both native soil Co, and applied Co. The most plausible interpretation of the data is that soils with high Mn contents strongly fix Co and, as a result, restrict uptake of native soil Co and show negligible responses to Co fertiliser treatment. However, the estimated soil Mn limits, above which plant responses to Co fertiliser appear unlikely, should be viewed with some caution. Extrapolation of the Mn limits from this glasshouse study to the field situation is probably unwise until corroborative field studies have been undertaken.

The considerable variation in soil Mn status in the soils used in this study was also considered responsible for the lack of an overall effect of soil pH on ryegrass Co concentrations. However, the detailed interactions between Co and Mn in soils are difficult to unravel because of the close association between these two elements, and to a lesser extent with Fe and Al (Li et al. 2001b).

Certainly, for soils with a large variation in Mn status, it appears that neither total soil Co, nor EDTA- or CaC_2-extractable Co can be used, without other information, to evaluate soil Co availability for plant uptake. Apart from soil Mn, the results from this study also suggest that Co availability to plants may also be influenced by organically-bound Co.

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