The effects of soil manganese status on the bioavailability of soil cobalt for pasture uptake in New Zealand soils

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Abstract

The effects of soil properties on the availability of cobalt (Co) for pasture uptake have been studied using a wide range of New Zealand soils. There is a strong positive correlation between total or EDTA-extractable Co and manganese (Mn) concentration. However glasshouse studies have shown that Co availability is inversely related to the Mn concentration. Across a wide range of soil groups, EDTA-extractable Co is a poor predictor of cobalt availability. $CaCl_2$-extractable Co was found to decrease with soil pH and was too pH sensitive to be a good predictor of Co availability. It is concluded that soil Mn plays a crucial role in soil Co status and has significant effects on plant Co uptake because of its involvement in the soil redox system and the scavenging properties of soil Mn oxides. Co deficiency is more likely to occur and Co fertiliser is less effective on soils with high Mn, especially under dry conditions.

Keywords: lime, pasture cobalt, soil cobalt, soil manganese, soil moisture, trace elements

Introduction

Adequate cobalt (Co) in pasture is essential for ruminant health in New Zealand pastoral agriculture (Andrews 1970). Since the late 1930s, when Co deficiency was diagnosed, many studies have been undertaken in New Zealand in attempts to find more convenient methods of assessing the Co status in soils at the soil group and/ or the farm level (Forbes 1976; Kidson 1937; McLaren *et al.* 1987; Metherell 1989; O'Connor *et al.* 1995; Sherrell 1990; Sherrell *et al.* 1990).

The current soil diagnostic method, 0.02M EDTA extraction, used by AgResearch is not particularly sensitive, and there are problems with its interpretation (O'Connor *et al.* 1995). Topdressing with Co fertiliser has been widely used to control Co deficiency (Andrews 1970; Sherrell *et al.* 1990). However variation in the efficacy and durability of Co topdressing to overcome Co deficiency can not be fully explained. An increasing incidence of Co deficient situations have been reported recently, even in areas which previously were believed not to have a Co problem (O'Connor *et al.* 1995).

Soil Mn plays a crucial role in the fate of soil Co because of the affinity of soil Mn oxides for Co (Adams *et al.* 1969) and its involvement in oxidation and reduction (redox) reactions. In soils, Mn is found in soluble Mn^{2+}, insoluble Mn^{3+} and Mn^{4+} (Mn oxides) oxidation states. The balance between these forms is controlled by the soil pH and redox status. Redox reactions are affected by soil moisture and biological activity. It has been hypothesised (Metherell 1989) that these factors are likely to affect the Co status of pasture. An ongoing research programme, carried out by Lincoln University and AgResearch and sponsored by Meat New Zealand, focuses on the effects of soil Mn on soil Co availability for pasture uptake. Using various soil chemical extractions, the impact of soil properties on Co availability over a wide range of New Zealand soils has been examined in glass house trials.

Materials and methods

1. Co and Mn in New Zealand Soils

Fifty-one surface and 45 sub-soil samples were collected from permanent grassland sites throughout New Zealand. Cobalt and Mn extracted by EDTA (0.02M) and $CaCl_2$ (0.05M) were determined together with total Co, Mn, iron (Fe) and aluminium (Al), soil organic carbon (C) and soil pH.

2. Pot trials in the glass house

Two pot trials were carried out separately in a glass house.

Pot Trial 1 was conducted to assess the effects of soil properties, added Co and soil moisture conditions, on the availability of Co. Topsoils (0–10 cm) from grassland sites throughout New Zealand were used for Pot Trial 1. Soils with (n=15) and without (n=18) Co treatment (350 μg $CoSO_4 \cdot 7H_2O$/kg) were kept at field capacity or 70% field capacity moisture levels after sowing with ryegrass seeds. Pasture Co and soil 0.05M $CaCl_2$-extractable Co and Mn, together with soil pH, were determined after the trial.

Pot Trial 2 was designed to assess the effects of soil pH and soil moisture conditions on the availability of soil Co for pasture uptake. Four topsoils (0–10 cm) with a wide range in native Mn and different soil physical and chemical properties

Table 1 Some chemical properties of the soils used in Pot Trial 2.

Soil Name	Soil Group	EDTA-Co(µg/g)	EDTA-Mn(µg/g)	$CaCl_2$-Co(µg/g)	$CaCl_2$-Mn(µg/g)	pH (initial)
Selwyn	Recent	0.68	26	0.105	8	5.21
Makarewa	Recent Gley	0.88	157	0.060	22	5.23
Kauroa	Allophanic	3.35	1464	0.011	67	5.38
Taupo	Pumice	0.62	99	0.055	19	5.31

Table 2 Linear correlation coefficients (r) between soil properties in topsoils.

	EDTA Co	$CaCl_2$ Co	Total Mn	EDTA Mn	$CaCl_2$ Mn	Total Fe	Total Al	Carbon	pH
Total Co	0.72*	0.04	0.77*	0.60*	0.27	0.72*	0.53*	0.00	0.25
EDTA Co		0.24	0.76*	0.78*	0.63*	0.34	0.24	-0.07	0.08
$CaCl_2$ Co			-0.10	-0.05	0.42*	-0.06	-0.24	-0.13	-0.53*
Total Mn				0.94*	0.50*	0.53*	0.56*	0.12	0.13
EDTA Mn					0.64*	0.32	0.43*	0.11	0.02
$CaCl_2$ Mn						0.07	0.12	0.17	-0.44*

*Significant at P < 0.01; n = 51

were collected (Table 1). Soils with and without lime treatment (4 g $Ca(OH)_2$/kg) were incubated for 2 months at field capacity moisture level. The soils were then split, and either maintained at field capacity or at saturated moisture level after sowing with ryegrass seeds. Soil 0.05M $CaCl_2$-extractable Co and Mn, and 0.02M EDTA-extractable Co, Mn, Fe and Al were determined together with pasture Co.

Analytical methods

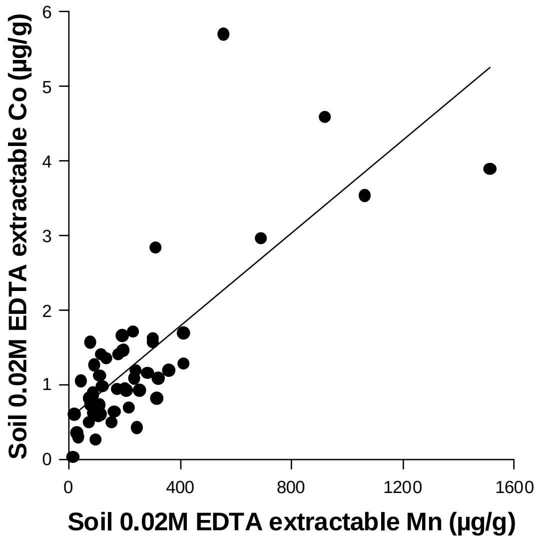
Mn, Fe and Al in soil extracts and digests, and Mn and Fe in pasture digests were determined directly by Flame Atomic Absorption Spectrophotometry. Co in EDTA extracts and digests was determined directly by Graphite Furnace Atomic Absorption Spectrophotometry (GFAAS). Co in $CaCl_2$ extracts and pasture digests was determined after extraction of the nitroso-R-complex with 4-methyl pentan-2-one (MIBK) by GFAAS (Poole 1980). Separate sets of standards were prepared for each of the chemical reagents. All extractions and analyses were carried out in duplicate.

Results and discussion

1. Co and Mn in New Zealand soils

Highly significant correlations were observed between Total Co and Total Mn, Fe and Al, and EDTA-extractable Co and Mn (Table 2). EDTA-extractable Co was correlated with Total, EDTA, $CaCl_2$-extractable Mn (Figure 1). It is obvious that a high proportion of the Co in soil is bound to Mn oxides (Childs 1975; Taylor & McKenzie 1966). $CaCl_2$-extractable Co and Mn were correlated with each other, and both were negatively correlated with soil pH (Figure 2). However $CaCl_2$-extractable Co was not significantly correlated with any other soil property (Table 2).

Figure 1 The relationship between soil 0.02M EDTA Co and 0.02M EDTA Mn in 51 topsoils.



Total Co values ranged from 0.44 to 14.6 µg/g (mean 5.33), EDTA-extractable Co from 0.04 to 5.69 µg/g (mean 1.31) and $CaCl_2$-extractable Co from 0.004 to 0.406 µg/g (mean 0.083). Soils developed from materials with low ferromagnesian mineral contents, such as pumice soils, usually have a low abundance of Co. Total Mn values ranged from 50 to 3208 µg/g (mean 640), EDTA-extractable Mn from 17 to 1514 µg/g (mean 248) and $CaCl_2$-extractable Mn from 6.25 to 129 µg/g (mean 48.6).

Table 3 Linear correlation coefficients (r) between pasture Co and soil properties in Pot Trial 1.

	Soil pH	$CaCl_2$ Co	$CaCl_2$ Mn	$(CaCl_2\ Mn)^{-1}$	EDTA Co	EDTA Mn	$(EDTA\ Mn)^{-1}$	EDTA Fe	Total Co	Total Mn	$(Total\ Mn)^{-1}$	Total Fe	Total Al
Pasture Co (No Co added)	0.14	-0.21	-0.62	0.85*	-0.64*	-0.45	0.79*	0.30	-0.78*	-0.48	0.72*	-0.57	-0.50
Pasture Co (Co added)	0.17	-0.19	-0.62	0.74*	-0.67*	-0.48	0.71*	0.19	-0.83*	-0.52	0.82*	-0.67*	-0.55

*Significant at P<0.01

However, there was no clear rela-tionship between soil Mn levels and soil orders.

Air-drying of samples, a common practice in most soil laboratories, caused a substantial increase in $CaCl_2$-extractable Co compared with fresh soil samples. One possible explanation for this phenomenon is that during the air drying processing, microbes in soils may be capable of coupling oxidation of organic C to reduction of soil Mn oxides, thus increasing the soluble and exchangeable Mn. Because soil Co has a close association with soil Mn oxides, reduction of Mn oxides will correspondingly increase easily extractable Co.

Figure 2 The relationship between soil pH and soil 0.05M $CaCl_2$ Co in 51 topsoils.

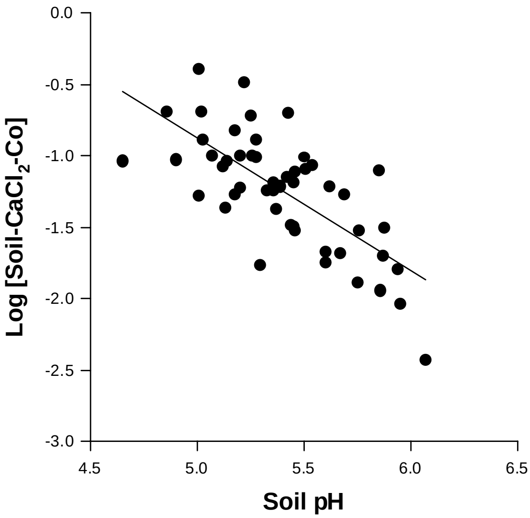
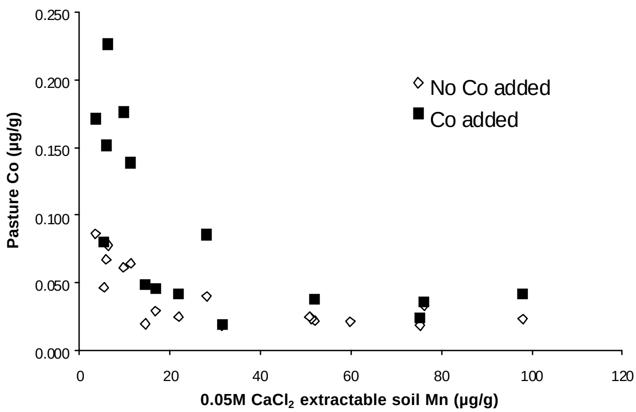


Figure 3 Effect of added Co fertiliser and soil Mn status, measured by 0.05M $CaCl_2$ extract, on pasture Co levels in Pot Trial 1.



2. Pot trials

Trial 1: There was no significant moisture effect between field capacity and 70% field capacity on pasture Co. Pasture Co contents, both with and without the Co treatment, had significant nega-tive correlations to total soil Co, 0.02M EDTA-extractable Co, 0.05M $CaCl_2$-extractable Mn, total soil Mn, Fe and Al, and 0.02M EDTA-extrac-table soil Mn (Table 3, Figure 3). There was a linear relationship between pasture Co and the inverse of each of the measures of soil Mn. The pasture Co results provided more evidence that acid digestion and/or strong extraction, such as EDTA, dissolves Mn fractions, along with Co that is not available to plants. For pumice soils, which have low native Mn and Co in their parent material, EDTA extraction would not introduce significant errors. In contrast EDTA extraction is a very poor indicator of Co availability in soils that have high Mn levels in their secondary min-erals.

There was almost no pasture Co response to Co fertiliser on the soils with high Mn concentration (Figure 3). The magnitude of the pasture Co response was also linearly related to the inverse of soil Mn status. It is concluded that soil Mn plays a crucial role in soil Co status and has significant effects on plant Co uptake.

Figure 4 Effect of lime, soil moisture status and soil groups on pasture Co in Pot Trial 2.

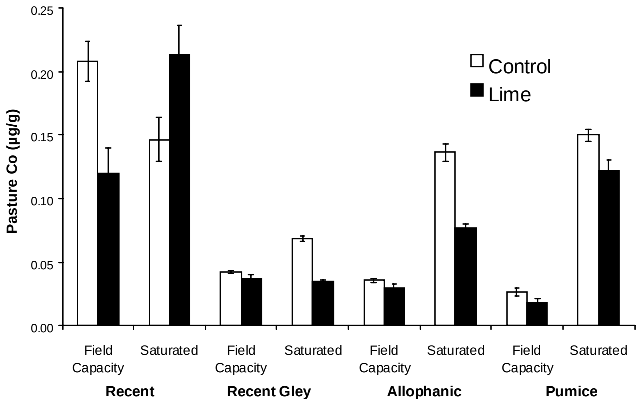
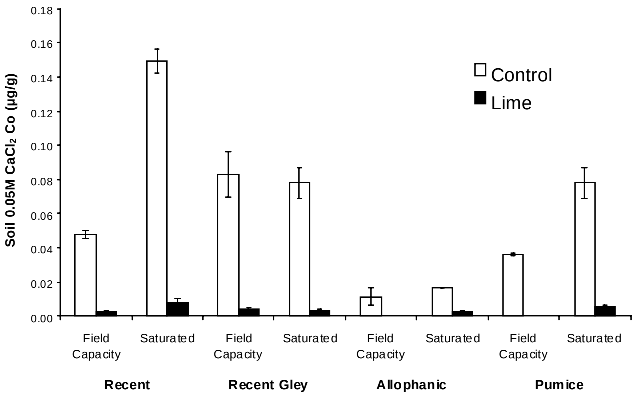


Figure 5 Effect of lime, soil moisture status and soil groups on 0.05M $CaCl_2$ extractable Co measured after harvest in Pot Trial 2.



Trial 2: Apart from the saturated recent soil, all soils showed the same pattern to lime treatment for pasture Co (Figure 4) and 0.05M $CaCl_2$-extractable Co (Figure 5). The lime treatment reduced 0.05M $CaCl_2$-extractable Co to less than 0.01µg/g. The reduction of pasture Co caused by increased pH was relatively less than for 0.05M $CaCl_2$-extractable Co. $CaCl_2$-extractable Co is thus too sensitive to pH to be used for prediction of plant Co. The pH buffer effect around the rhizosphere may be a reasonable explanation. Pasture Co and 0.05M $CaCl_2$-extractable Co from soils under saturated moisture conditions were generally higher than from soils at field capacity. Mn oxides would be reduced under saturated moisture conditions and thus release Co^{2+} associated with them. A linear relationship between pasture Co and the inverse of soil EDTA extractable Mn, with a different slope for limed soils, was found for soils held at field capacity, but the relationship did not hold under saturated conditions.

Conclusions

In New Zealand soils, there is a close association between total and EDTA-extractable Co and soil Mn status. Soil Co is significantly influenced by soil Mn status through the strong fixing ability and the redox reactions of Mn oxides. As a result of the chemical reactivity of Mn oxides, and the soil microbial involvement in the Mn redox system, soil Mn status can change dramatically over short distances and times.

The efficacy of Co fertiliser topdressing is also largely controlled by soil Mn. On soils with high Mn, Co fertiliser has limited effectiveness in raising pasture Co concentrations.

If soil Mn is high, the 0.02M EDTA extraction, which is currently used by AgResearch as a soil Co assessment in farm surveys, over-estimates the potential Co available for pasture uptake. Because EDTA is strong enough to dissolve the Mn oxides along with the soil organic matter, this obscures the pH effects on soil Co availability. However $CaCl_2$-extractable Co is too sensitive to soil pH to be a suitable extractant.

In the glasshouse $CaCl_2$-extractable Mn was the best predictor of Co availability. Saturated soil conditions generally increased pasture Co and lime reduced pasture Co.

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