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Cobalt and nickel accumulation in *Nyssa* (tupelo) species and its significance for New Zealand agriculture

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Abstract Ninety-seven leaf samples taken from three cobalt-accumulating species of *Nyssa* (tupelo) growing at various localities in New Zealand were analysed for Co and Ni to examine the range of Co and Ni concentrations found in New Zealand specimens, as well as to determine whether their Co content was a measure of the Co status of the soils. A further aim was to establish whether leaves could be used as a feed supplement to sheep and cattle in order to avoid Co deficiency in farm animals. Maximum Co and Ni concentrations were 95 and 32 $\mu g\ g^{-1}$ (dry mass) in leaves of *N. sylvatica* with geometric means of 7.1 and 4.0 $\mu g\ g^{-1}$, respectively. Comparable values were obtained for *N. aquatica* and *N. sinensis*. Bioaccumulation coefficients (BAC, i.e., plant/soil Co or Ni quotients) were 4–6 times higher for Co than for Ni and showed a disproportionately high uptake of Co compared with Ni. BAC values increased exponentially with decreasing Co concentrations in the soil, thus highlighting the possibility of using *Nyssa* to recover Co from soils impoverished in this element. It was calculated that leaf fall from three *Nyssa* trees, when used as a feed supplement, may provide sufficient Co to alleviate Co deficiency for up to 10 sheep, though this procedure will require further study before being recommended unequivocally.

Keywords *Nyssa sylvatica*; *Nyssa aquatica*; *Nyssa sinensis*; cobalt; nickel

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INTRODUCTION

It has been known for well over 40 years that the American tree *Nyssa sylvatica* var. *sylvatica* (tupelo or black gum), as well as its other subspecies, can accumulate relatively high concentrations of Co. This initial discovery was made by Beeson et al. (1955) who reported that *Nyssa sylvatica* var. *biflora* (swamp black gum) contained up to 31 $\mu g\ g^{-1}$ Co (dry mass) compared with <0.1 $\mu g\ g^{-1}$ in other plants collected from the same sites. Kubota et al. (1960) reported up to 845 $\mu g\ g^{-1}$ Co in the same species compared with a maximum of 0.4 $\mu g\ g^{-1}$ in accompanying broom sedge and suggested that this tree might be an indicator of the Co status of American soils.

The use of *Nyssa sylvatica* and its varieties to assess the Co status of soils was continued by the work of Shacklette et al. (1970) and Connor & Shacklette (1975) who found up to 30 $\mu g\ g^{-1}$ Co (dry mass) in leaves of this species. A detailed survey of the natural abundances of Co and Ni in species and varieties of *Nyssa* was carried out by Brooks et al. (1977) who determined the concentrations of both elements in leaves of 346 wild specimens growing in North America and Asia (Table 1).

The original purpose of the studies by Kubota & Lazar (1958) and by Kubota et al. (1960) had been to establish whether the Co content of *Nyssa* species would indicate the Co status of the accompanying soils. They concluded that the Co content of these trees was indeed a function of soil type, and that, in some but not all soils, impeded drainage increased Co uptake.

The present study had a threefold purpose: establishing the range of Co (and geochemically related Ni) concentrations in *Nyssa* species growing in New Zealand; establishing the degree to which the Co and/or Ni content of leaves of these plants is an indication of the Co/Ni status of the soils; determining whether leaves of the deciduous *Nyssa* trees might be used as a forage additive, particularly in parts of New Zealand where Co deficiency is a serious problem in animal nutrition.

MATERIALS AND METHODS

A tree nursery from the Nelson area of South Island supplied us with a list of all people who had bought *Nyssa* saplings from them in 1990. These plants would now be about 10 years old. We wrote to 94 such customers asking for a small number of leaves together with soil samples taken at least 2 m away from the tree at a depth of about 10 cm. We received 49 replies enclosing a total of 97 leaf samples of three species of *Nyssa* together with their associated soils. The localities of these samples are shown in Fig. 1.

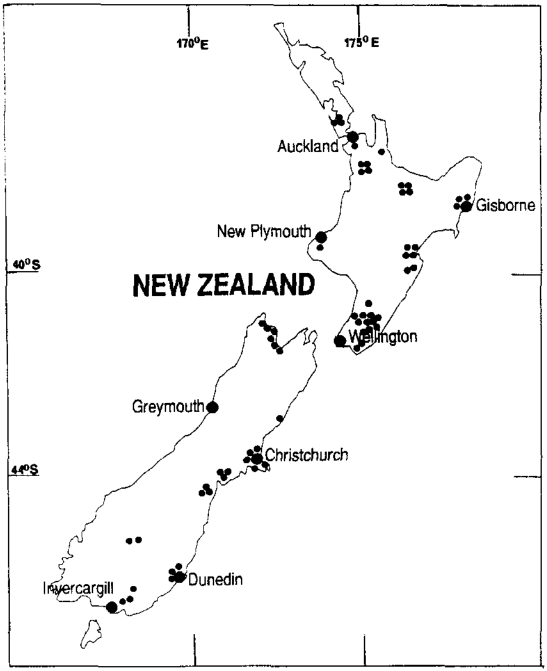

Fig. 1 Approximate sampling locations of leaf samples of *Nyssa* species and their associated soils.

Leaf analysis

Leaves were washed and dried at 70°C overnight. Dry samples (c. 0.1 g) were placed in 10-ml borosilicate test tubes and ashed overnight at 500°C. The ashed samples were redissolved in 5 ml of warm 2 *M* HCl and the tubes shaken to assist dissolution. Cobalt and Ni concentrations in the solutions were determined in most cases by flame atomic absorption spectrometry (FAAS) using a GBC 904 instrument. When the elemental concentrations were too low for quantification by FAAS, the two elements were determined by the more sensitive technique of graphite furnace atomic absorption spectrometry (GFAAS) using a GBC 909/System 3000 instrument.

Soil analysis

Soils were treated in two different ways. For total Co and Ni concentrations, 0.5-g soil samples were digested with 10 ml of a 1:1 HNO_3:HF mixture in 50-ml polypropylene beakers and taken to dryness over a hot water bath (100°C). The residues were redissolved in 10 ml of 2 *M* HCl as above. For extractable Co and Ni, 1-g soil samples were shaken with 10 ml of 1 *M* ammonium acetate (pH 7.0) in polypropylene sealed vials placed in an end-over-end rotary shaker. Both sets of soils were analysed as above by FAAS and GFAAS. After drying at

Table 1 Cobalt and nickel concentrations ($\mu g\ g^{-1}$ dry mass) in leaves of wild specimens of Nyssaceae. Data from Brooks et al. (1977).

		Cobalt		Nickel		
	n	Mean	Max.	Mean	Max.	Co/Ni
Nyssa sylvatica var. *sylvatica*	91	15	530	7	250	2.0
N. sylvatica var. *biflora*	41	6	205	3	53	1.7
N. aquatica	36	3	65	4	11	1.9
N. ogeche	25	8	39	2	17	3.4
N. sinensis	18	23	120	3	107	1.8
N. javanica	3	9	16	6	21	1.4

105°C for 16 h, the organic matter content of soils (l.o.i., loss on ignition) was determined from the weight loss after ignition at 500°C for 4 h.

Correlation analysis was carried out on 11 variables. Where appropriate the data were transformed logarithmically when distributions were lognormal.

RESULTS AND DISCUSSION

Characteristics of cobalt and nickel concentrations in New Zealand Nyssaceae

The concentrations reported by us (Table 2) for both Co and Ni in all three species are appreciably lower than those in North American wild plants (Table 1). It must be remembered that all of our samples represented exotic imports not found naturally at the sites from which they were sampled.

Although maximum Ni concentrations in *Nyssa sylvatica* specimens were less than half those of Co, the plant/soil quotient presents quite a different picture. For Co the geometric means (used because the data were lognormally distributed) were 1.70, 2.05, and 10.3 μg g^{-1} for *N. sylvatica*, *N. aquatica*, and *N. sinensis*, respectively (Table 2). The corresponding maximum values were 300, 2.4, and 45 μg g^{-1}. Corresponding data for Ni in the same three species were means of 0.4, 0.33, and 25 μg g^{-1} with maxima of 6, 0.40, and 117 μg g^{-1}. The values for *N. sinensis*, however, were non-significant because of the small size of the sample (n = 3). It is clear that both *N. sylvatica* and *N. aquatica* are able to accumulate Co selectively over Ni by a factor of about 4–6.

Loss on ignition (l.o.i.) results show that *N. aquatica* appears to have been planted in soils with a somewhat higher humus content (Table 2). This

Table 2 Cobalt and nickel concentrations (μg g^{-1} dry weight) in plants and soils. L.o.i., loss on ignition at 500°C; A.m., arithmetic mean; G.m., geometric mean.

Element and material	A.m.	G.m.	Median	Min.	Max.
Nyssa sylvatica (n = 86)					
Co in leaves	12.2	7.1	7.2	1.0	95
Ni in leaves	5.6	4.0	4.3	0.8	40
Co/Ni in leaves	2.2	1.8	1.7	1.3	2.4
Total Co in soils	6.0	4.1	5.2	0.1	36
Total Ni in soils	11.3	8.4	10.0	1.3	32
Co/Ni in soils	0.5	0.5	0.5	0.08	1.1
Extractable Co in soils	0.1	0.06	0.08	0.003	37
Extractable Ni in soils	0.15	0.06	0.06	0.001	3
L.o.i in soils (%)	13.3	11.8	11.4	5.1	23
Co plant/soil	8.4	1.7	1.8	0.1	300
Ni plant/soil	0.7	0.4	0.4	0.01	6
Nyssa aquatica (n = 8)					
Co in leaves	22.6	4.2	28.4	0.7	61
Ni in leaves	3.11	2.8	2.7	1.0	5
Total Co in soils	9.9	4.5	3.7	1.0	25
Extractable Co in soils	0.3	0.3	0.3	0.1	0.4
Extractable Ni in soils	0.2	0.3	0.2	0.1	0.2
L.o.i in soils (%)	18.9	18.3	22.5	13.4	23
Co plant/soil	2.08	2.05	1.9	1.87	2.4
Ni plant/soil	0.20	0.33	0.13	0.07	0.4
Nyssa sinensis (n = 3)					
Co in leaves	17.2	13.5	12.6	5.4	37
Ni in leaves	6.16	4.94	3.4	3.1	12
Total Co in soils	2.15	1.10	2.6	0.7	4.8
Total Ni in soils	3.9	0.59	6.0	0.1	9.4
Extractable Co in soils	0.18	0.36	0.06	0.06	0.08
Extractable Ni in soils	0.05	0.25	0.04	0.03	0.07
L.o.i in soils (%)	16.8	16.6	16.8	13.4	20
Co plant/soil	20.3	10.3	14.2	1.75	45
Ni plant/soil	55	25	47	0.32	117

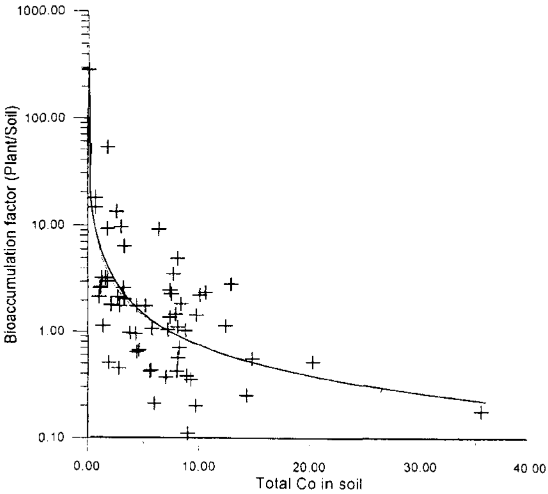

Fig. 2 Bioaccumulation factors (plant/soil elemental quotient) for Co in leaves of *Nyssa sylvatica*.

is to be expected because this species favours poorly drained sites which usually have a higher organic content in the substrate.

There is a tendency for bioaccumulation coefficients (BAC), i.e., plant/soil elemental concentrations quotients, to increase in magnitude as the elemental content in the soil decreases. This is demonstrated in Fig. 2 from which it will be seen that BAC values decrease from c. 200 for a Co concentration of 1 $\mu g\ g^{-1}$ in the soil down to just under 0.2 when the metal concentration reaches 37 $\mu g\ g^{-1}$ in the soil. This finding is of some importance because it highlights the possibility that *N. sylvatica* might have some potential to recover significant amounts of Co from soils containing low levels of this element.

Concentrations of Co and Ni in soils are in most cases similar to those expected in non-ultramafic soils (ultramafic soils are high in Ni, Co, and Mg). Mean values for Co were 4.1 $\mu g\ g^{-1}$ with a minimum and maximum of 0.1 and 36 $\mu g\ g^{-1}$, respectively. Kidson (1937) reported a range of 0.3–380 $\mu g\ g^{-1}$ with soils containing <2 $\mu g\ g^{-1}$ being associated with Co deficiency in animals. Our mean, minimum, and maximum values for Ni were 8.4, 1.3, and 32 $\mu g\ g^{-1}$, respectively. The highest values for Ni and Co were not associated with ultramafic soils and were more likely a result of fertilising with "serpentine superphosphate" which has elevated concentrations of both elements.

The Co content of leaves of *Nyssa sylvatica* was unrelated to the total and the extractable soil Co (Table 3). There was a very highly significant link between the Co in leaves and their Ni concentration. This was to be expected because of the geochemical association between these two elements as well as their association in serpentine superphosphate fertilisers. Of major importance is the highly significant inverse relationship between the Co content of leaves and the value of the BAC for this element (Table 3). This is also shown in Fig. 2 and is of importance in showing that *Nyssa sylvatica* has a good potential to extract Co from soils with low abundances of this element. A similar pattern can be observed for Ni. The BAC values of both elements are mutually correlated to a very highly significant degree. Both Co and Ni in soils were very highly correlated because of their geochemical similarities. This was also the case for the extractable fractions of both elements in soils when correlated against each other and with their total concentrations in soils.

Significance for New Zealand agriculture

Although Kubota et al. (1960) reported that *Nyssa sylvatica* might be used to indicate the Co status of North American soils, this is hardly the case for the New Zealand environment. There was no significant relationship between the Co content of leaves of this species and the Co status of the soil. The reason is not hard to establish. The North American trees were almost without exception growing in their natural environment, whereas the trees used in this study had been artificially planted, probably in disturbed, translocated, or fertilised soils. The addition of serpentine superphosphate with its high

Table 3 Correlation analysis of data for soils and leaves of *Nyssa sylvatica*. NS, not significant; *, $P < 0.05$; **, $P < 0.01$; ***, $P < 0.001$; -, inverse relationship; A, total Co in soil; B, extractable Co in soil; C, total Ni in soil; D, extractable Ni in soil; E, Co in leaves; F, Ni in leaves; G, Co bioaccumulation coefficient; H, Ni bioaccumulation coefficient.

	A	B	C	D	E	F	G
B	NS						
C	***	*					
D	**	**	**				
E	NS	NS	NS	NS			
F	NS	NS	NS	*	***		
G	–***	NS	NS	–*	***	***	
H	–**	–*	-***	NS	*	***	***

Co and Ni content or superphosphate with added Co will certainly have given rise to soils of different composition to the local undisturbed types.

The most significant finding from this present report is that there is a real possibility that litter from this tree might be used as a feed additive to stock grazing Co-deficient pastures that are found throughout New Zealand, but particularly in the Central Volcanic Plateau. It has been established (Andrews et al. 1958; Clark & Millar 1983) that pastures containing a minimum of 0.11 and 0.08 $\mu g\ g^{-1}$ (ppm) Co in dry mass will provide sufficient of this element for sheep and cattle, respectively.

Normal pastures contain on average about 0.15 $\mu g\ g^{-1}$ Co. However, in pastures on soils formed from the Taupo and Kaharoa ash showers, the levels are far lower (c. 0.04 $\mu g\ g^{-1}$) and require an admixture of Co either as the sulphate or as an additive to superphosphate. When added directly, cobalt sulphate ($CoSO_4.6H_2O$) is usually used at a rate of 350 g ha^{-1} yr^{-1} which translates to a yearly addition of about 80 g ha^{-1} of Co metal (During 1984). It is known that this amendment of 80 g ha^{-1} yr^{-1} removes all signs of Co deficiency in animals and is therefore a yardstick for a desired level of application. Recently, the less expensive option of injecting slow-release cobalt preparations into stock has replaced the fertilisation of pasture with Co.

A mature specimen of *Nyssa sylvatica* produces about 40 kg of leaf litter annually. Assuming that this litter contains 5 $\mu g\ g^{-1}$ (mg kg^{-1}) Co (the mean of our experiments was in fact 7 $\mu g\ g^{-1}$), the leaves of each tree could provide 200 mg of Co. Clearly it would be impracticable to grow enough trees to add their leaves to the soil as a direct amendment. However, another approach might be employed.

A ewe and her lamb will consume about 550 kg of dry matter in one year. This is 5.5 t ha^{-1} at a stocking rate of 10 units ha^{-1}. Assuming that this feed is from a normal pasture with 0.15 $\mu g\ g^{-1}$ Co (Andrews 1966), it would contain 825 mg of Co. Assuming that we are dealing with an impoverished pasture with only 0.06 mg kg^{-1} Co (Andrews 1966), this would provide only 330 mg of this element. There is therefore a deficiency of 495 mg of Co that could be more than supplied by only three trees, each with 5 $\mu g\ g^{-1}$ Co in its leaves.

The palatability of forage amended with *Nyssa* leaves remains to be determined and this question will not be answered without further extensive research. However, it can be shown from the above calculation that 100 kg of *Nyssa* leaf material (containing 5 $\mu g\ g^{-1}$ Co) would need to be added to the 5.5 t ha^{-1} of cobalt-deficient forage to provide the additional required 500 mg of Co. This amounts to only 1.8% by weight of the original feed and is not likely to make it unacceptable to sheep. It is also highly unlikely that it will ever be possible to inadvertently supply a toxic dose of Co from *Nyssa* leaves since animals are often supplied directly with Co pellets, "bullets", or tablets introduced directly into the animal (Underwood 1981) at a rate greatly in excess of the likely intake from *Nyssa* leaves.

The above calculations have considered mainly sheep, which are more susceptible to Co deficiency than are cattle. Cattle, especially calves, are more sensitive to Co toxicity than are sheep (Dickson & Bond 1974), but again the contemplated *Nyssa*-based dosages are not likely to even approach levels of toxicity commonly reported for Co and Ni (150 $\mu g\ g^{-1}$ and 250 $\mu g\ g^{-1}$, for example) as the highest values found in *Nyssa* leaves were only 90 $\mu g\ g^{-1}$ and 40 $\mu g\ g^{-1}$, respectively.

The above discussion highlights two very different approaches. Our proposals involve direct administration of Co in feed compared with the wasteful conventional approach of adding a large excess of Co and hoping that sufficient of it remains in the soil or is eaten by the animals to ensure no symptoms of Co deficiency. The trees could be planted as lightly dispersed individuals (e.g., 3 ha^{-1}) within a field or as boundary markers. We intend revisiting some trees sampled here in order to elucidate the factors leading to large recoveries of Co in *Nyssa* leaves.

It is envisaged that dried *Nyssa* leaves be collected at leaf fall in April/May and added to hay or silage either manually or mechanically. The mechanics of such an operation are now under investigation and beyond the scope of this paper. However, the fundamental problem remains as to whether farmers would be prepared to go to the trouble of planting trees, waiting a few years, and then adding *Nyssa* to extra feed supplied during the year. For organic farmers, however, the proposed scenario would likely be attractive, and for both groups of agriculturalists the *Nyssa* would certainly be pleasing aesthetically as it is one of the world's most spectacular provider of autumn colours.

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