Ref 312 0247

EXTRACTABILITY OF NICKEL ADDED TO SOILS AND ITS CONCENTRATION IN PLANTS[1]

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Received April 2, 1969

ABSTRACT

The effect of Ni pretreatments on the yield and concentration of Ni in oats and alfalfa grown in four soils in pot tests varied with the rate of added Ni, with lime and phosphate treatments, and with soil properties, notably pH and organic matter content. The concentrations of Ni in the crops showing repressive effects of added Ni were at least 60 ppm in the oat grain, 28 ppm in the oat straw, and 44 ppm in the alfalfa. The amounts of soil-extractable Ni and the concentrations of Ni in the plants were reduced by liming of the acid soils and they tended to be increased by addition of phosphate. The effects of the Ni pretreatments on growth were less severe in a neutral soil and in one containing considerable organic matter than in the others.

INTRODUCTION

Most investigations of Ni in soils and its effect on plant growth have resulted from observations of poor growth on soils derived from basic rocks or serpentine (2, 4, 5). Although Ni is used in certain fungicides and is usually present in pulverized serpentine, which may be used as a source of available Mg (1), there is little recorded evidence of soil pollution from these sources. In soils near Ni mining areas, however, toxic levels of Ni might be expected to occur. Since the toxic effect of Ni varies markedly with plant species (9, 14) and the toxic level in soils varies with its properties (8, 10), it is difficult to indicate critical levels for either soils or plants. According to Mitchell (8), soils derived from basic igneous rocks or argillaceous sediments may be expected to contain from 50 to 500 ppm Ni, whereas less than 50 ppm is normal in soils from sandstones, limestones and acid igneous rocks.

Nikolic (10) reported that addition of nickel chloride reduced the yield of oats in a pot experiment with a Podzol but not with a Calcareous Black Earth (Tchernoziem) soil. Vergnano and Hunter (14) found that oat leaves from plants grown in solutions with 0 to 30 ppm Ni contained from 7 to 92.5 ppm of this element.

The purpose of this investigation was to assess the effect of soil properties and additions of P and lime on the extractable Ni in soils pretreated with Ni, and the yield and Ni concentration of plants grown in pot tests.

MATERIALS AND METHODS

Soils

Four samples of soil varying in pH and organic matter were collected in the fall of 1967 from experimental sites at Ottawa. Sample 1 was a Grenville sandy loam, and sample 2 was a Granby sandy loam, whereas samples 3 and 4 were Uplands sand. They are described elsewhere (7) but, for convenience, some properties of the soils are given in Table 1.

Greenhouse Experiment

Samples were air-dried and passed through a 1.25-mesh screen. Nickel chloride was mixed with 2268 g of air-dry soil in plastic pots at rates of 0, 20, 50, 100

[1]Contribution No. 306.

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and 500 ppm Ni. After 1 month of moist incubation, lime and phosphorus treatments were mixed with the soils. The treatments were control, P, lime, and lime + P, except that soil No. 1 received no lime. P as $CaH_4(PO_4)_2 \cdot 2H_2O$ was supplied at the rate of 500 ppm, whereas lime (precipitated $CaCO_3$) was added at a rate of 3750 ppm to soil 2, 1000 ppm to soil 3, and 3000 ppm to soil 4. The soils were kept moist at about field capacity for another month, after which time 500 ppm of a 5–10–10 fertilizer was mixed with the soil in all pots prior to seeding oats. The treatments were randomized and the experiment was replicated four times. An additional series of the treated soil was incubated moist for 6 months and then sampled, air-dried, sieved and retained for analyses. The oat grain, tops and roots were harvested after 110 days. Then alfalfa was seeded and alfalfa tops and roots were harvested after 83 days. The plant samples were oven-dried, ground in a Wiley mill and retained for analysis. Before analysis, two composite samples for each treatment were prepared by combining material from replication 1 with that from 2, and material from replication 3 with that from 4.

Laboratory Analyses

The pH of the samples was determined by glass electrode using a 1:1 soil: water ratio, and soluble P was determined by the $NaHCO_3$ method. Extracts of Ni in the soils were obtained (*a*) by leaching with 1 *N* neutral NH_4OAc and (*b*) by equilibrating the samples in 0.1 *M* $CaCl_2$. Ten grams of soil were extracted with 80 ml of 1 *N* neutral NH_4OAc after allowing the suspensions (1 soil: 2 NH_4OAc) to stand overnight. Twenty-five grams of soil were shaken in 50 ml 0.1 *M* $CaCl_2$ overnight. The soil-NH_4OAc suspensions were filtered with suction using Whatman No. 42 paper, whereas the soil-$CaCl_2$ suspensions were centrifuged and then filtered. The Ni in the extracts was determined without further preparation by atomic absorption (Techtron AA3).

The plant material was ashed overnight at 500°C and treated twice with hot 3 *N* HCl. Ni in these extracts was determined by atomic absorption and phosphorus by the vanadate method. The amounts of Ni found in the Ni-treated samples were corrected for the smaller amounts obtained for the corresponding control where Ni had not been added.

RESULTS

Soil Properties and Extractable Ni

The differences in pH and organic matter content of the samples (Table 1) provide an opportunity to assess these properties in relation to soluble Ni.

Table 1. Some properties of the soils

Property	Soils 1	2	3	4
pH (1:1 soil:water ratio)	7.8	6.4	6.1	5.7
Total N, %	0.15	0.65	0.05	0.15
Organic matter, %	4.0	21.2	1.4	4.1
Cation exchange capacity, meq/100 g	13.0	61.7	6.0	11.7
Base saturation, %	100	76	42	49

The pH of the incubated soils decreased slightly upon addition of phosphate in the presence of lime, and usually upon addition of Ni at the highest rate (Table 2). There was a tendency for addition of Ni to decrease the amount of soluble P in the soils, but in many instances the differences were small.

Table 2. pH and soluble phosphorus in the soils following incubation

Soil and treatment	pH			$NaHCO_3$-soluble P (ppm)	
	Ni pretreatment (ppm)			Ni pretreatment (ppm)	
	0	50	500	0	500
Soil 1					
0	7.6	7.6	7.5	28	28
P	7.3	7.3	7.0	302	266
Soil 2					
0	6.1	6.1	5.9	28	25
Lime	6.6	6.7	6.4	26	23
P	6.0	6.1	5.9	81	78
Lime + P	6.3	6.3	6.3	112	66
Soil 3					
0	5.8	5.6	5.1	19	11
Lime	6.8	6.3	5.9	17	17
P	5.7	5.6	5.2	149	144
Lime + P	6.4	6.2	5.8	161	99
Soil 4					
0	5.3	5.3	4.9	35	33
Lime	6.6	6.4	6.2	35	30
P	5.2	5.1	4.9	172	155
Lime + P	6.3	6.3	5.8	176	245

The amounts of extractable Ni varied with the pH and organic matter content of the soils (Table 3). For example, at the highest rate of added Ni (500 ppm) the amounts of Ni extracted from soils by 1 *N* NH_4OAc and 0.1 *M* $CaCl_2$ were in the following order: soil 1 < soil 2 < soil 4 < soil 3. This was in accord with the relatively high pH of soil 1, the relatively high organic matter content of soil 2, and the higher amount of organic matter in soil 4 than in soil 3. Advancing the pH of the acid soils by liming gave reductions in the amounts of extractable Ni, particularly in soils 3 and 4. On the other hand, addition of P usually increased the amounts of extractable Ni and the differences were marked, particularly where lime was applied to soils 3 and 4.

Yields of Oats and Alfalfa

The effects of added Ni on the yields of oats and alfalfa varied with the soils and crops (Table 4). Yields on soils 1 and 2 were not affected appreciably by Ni except for reduction in alfalfa at the high rate (500 ppm Ni). On soils 3 and 4, however, there was no growth of either oats or alfalfa when Ni was added at the high rate. Furthermore, the yield of oats was depressed by addition of 100 ppm Ni in soil 3, and the yield of alfalfa by no more than 50 ppm of added Ni in both of these soils. Other data showed that the effect of Ni on root growth was similar to that reported for the above-ground

Table 3. Extractable nickel in the soils (ppm) following incubation

Soil and treatment	1 *N* NH_4OAc			0.1 *M* $CaCl_2$	
	Ni pretreatment (ppm)			Ni pretreatment (ppm)*	
	0	50	500	50	500
Soil 1					
0	2.6	3.2	14	0.3	3
P	1.6	4.2	29	0.6	13
Soil 2					
0	< 1.0	2.4	31	0.9	30
Lime	< 1.0	2.4	28	0.6	17
P	< 1.0	2.4	37	0.9	33
Lime + P	< 1.0	2.4	35	0.6	23
Soil 3					
0	n.d.	9.3	228	19.8	272
Lime	< 1.0	3.7	94	4.8	112
P	n.d.	12.7	268	21.4	311
Lime + P	< 1.0	6.5	186	10.1	206
Soil 4					
0	n.d.	5.4	164	17.0	240
Lime	n.d.	1.6	59	2.4	76
P	n.d.	4.8	175	17.8	295
Lime + P	n.d.	2.6	133	4.8	159

*Ni was not detected (n.d.) in control samples receiving no Ni.

parts of the plants. This variation between soils with respect to the effects of Ni on plant growth was in accord with the amounts of extractable Ni in the soils (Table 3) and with soil properties (Table 1).

Where no Ni was added, lime had no apparent effect on yield except for small differences in the yield of alfalfa on soils 3 and 4. There were several instances, however, where liming tended to repress the detrimental effect of Ni in soils 3 and 4. Addition of P had no consistent effect on growth. With 500 ppm Ni on soil 1, P gave a reduction in the yield of oats, but in several instances it tended to repress the effect of Ni in soils 3 and 4, as did lime.

Ni Content of Oats and Alfalfa

Addition of Ni increased the concentrations of Ni in both oats and alfalfa (Table 5). With few exceptions, the oat grain contained more Ni than did the straw. In most of the comparisons, addition of P increased the Ni content of the plants. Lime lowered the Ni concentration in oats and alfalfa in soils 3 and 4 but there was no consistent evidence of this effect in the plants grown in soil 2. The concentration of Ni in the plants varied between soils. At the 50-ppm rate of Ni, the order of magnitude for the soils was soil 2 < soil 1 < soil 4 < soil 3. These variations were in accord with variations in organic matter content and pH of the soils.

In general, the effects of lime and P on Ni concentration in the plants were in accord with their effect on amounts of soluble Ni in the soils (Table 3). It is interesting to note that there was a slight decrease in P content of the crops with increasing rates of Ni (Table 6). This lower P content was in

Table 4. Yield of oats and alfalfa

Soil and treatment	Oat grain (g/pot)					Oat straw (g/pot)					Alfalfa tops (g/pot)				
	Ni pretreatment (ppm)					Ni pretreatment (ppm)					Ni pretreatment (ppm)				
	0	20	50	100	500	0	20	50	100	500	0	20	50	100	500
Soil 1															
0	6.5	5.8	6.6	5.7	6.9	7.5	7.7	7.7	7.5	8.2	1.9	2.9	2.4	2.7	0.3
P	6.5	6.7	6.9	7.1	4.8	9.2	8.7	8.9	8.8	6.7	2.2	2.4	2.1	2.4	0.4
SE, mean 4			0.4					0.3					0.2		
Soil 2															
0	9.2	8.5	8.4	8.6	8.9	11.0	11.1	10.5	10.7	10.5	4.3	4.9	4.5	4.1	1.8
Lime	8.1	8.9	7.6	7.7	7.9	10.8	10.2	10.3	10.0	9.6	3.4	4.4	4.0	3.7	0.9
P	9.8	9.3	9.5	8.7	9.8	11.6	11.1	10.6	11.6	10.5	4.8	5.3	6.0	4.9	1.1
Lime + P	9.7	9.6	9.5	8.7	9.3	11.7	10.7	11.1	10.5	10.4	4.3	4.9	5.1	4.5	2.9
SE, mean 4			0.4					0.3					0.3		
Soil 3															
0	2.6	3.4	1.6	—	—	7.0	6.3	2.6	—	—	1.0	0.6	<0.1	—	—
Lime	2.7	3.4	2.9	1.8	—	6.6	5.9	6.7	7.1	—	1.4	2.3	0.9	—	—
P	3.9	4.1	3.8	—	—	7.6	7.3	5.9	—	—	2.0	2.5	<0.1	—	—
Lime + P	4.0	4.1	3.7	2.0	—	7.4	7.3	7.1	5.2	—	2.2	3.5	0.4	—	—
SE, mean 4			0.2					0.3					0.2		
Soil 4															
0	3.3	4.0	4.4	3.8	—	7.6	7.3	6.7	4.2	—	1.9	1.9	0.6	—	—
Lime	3.2	4.7	4.8	4.4	—	7.3	6.0	7.2	7.1	0.4	2.7	2.9	3.3	2.2	—
P	3.9	4.8	4.6	5.7	—	7.1	6.8	7.8	6.2	—	2.9	3.2	1.1	—	—
Lime + P	3.6	4.4	4.7	5.5	—	7.9	7.3	7.6	7.3	—	3.8	3.9	3.8	2.7	—
SE, mean 4			0.3					0.3					0.3		

Table 5. Ni content of oats and alfalfa, ppm

Soil and treatment	Oat grain			Oat straw			Alfalfa tops		
	Ni pretreatment (ppm)			Ni pretreatment (ppm)			Ni pretreatment (ppm)		
	50	100	500	50	100	500	50	100	500
Soil 1									
0	16.6	20.2	67.7	1.7	2.2	13.6	11.6	15.6	64.2
P	21.4	33.9	77.1	4.2	9.6	28.2	14.8	25.7	73.4
SE, mean 2		2.5			2.5			1.3	
Soil 2									
0	13.9	23.5	65.6	3.3	5.2	25.1	5.3	11.1	51.5
Lime	11.5	19.6	75.9	1.1	5.2	26.0	3.8	9.4	61.1
P	14.0	23.0	81.2	6.6	6.5	32.6	4.9	13.0	76.6
Lime + P	14.9	20.3	78.9	1.8	5.4	31.0	6.1	13.3	63.0
SE, mean 2		2.4			2.7			3.2	
Soil 3									
0	60.2	—	—	42.3	—	—	78.0	—	—
Lime	38.1	69.1	—	11.0	32.3	—	43.6	—	—
P	65.5	—	—	34.7	—	—	99.5	—	—
Lime + P	64.5	69.8	—	20.3	36.6	—	77.0	—	—
SE, mean 2		9.9			1.8			4.6	
Soil 4									
0	55.8	63.9	—	21.7	45.8	—	63.8	—	—
Lime	32.2	52.6	—	14.6	21.1	—	30.5	45.1	—
P	73.5	71.3	—	26.9	35.9	—	67.9	—	—
Lime + P	41.9	68.2	—	12.8	25.3	—	39.8	60.6	—
SE, mean 2		3.5			2.7			2.8	

accord with the tendency for soluble P to decrease slightly in the soils at the highest rate of applied Ni (Table 2). Nevertheless, a Cl–P antagonism may have affected the concentration of P in the plants, since Ni was added in the chloride form.

Critical Levels

Although the data reported herein are not adequate to formulate critical levels of Ni in the plants and soils, nevertheless, some observations are warranted. The relationships between Ni levels in the plants and soils and the effect of Ni pretreatments on yields were found to vary between soils, with amendments added, and with the crop grown. There was evidence of a repressive effect

Table 6. Phosphorus content of oats and alfalfa in relation to nickel pretreatments, %

Ni pretreatment (ppm)	Oats*				Alfalfa*	
	Grain		Straw		Tops	
	No P	P	No P	P	No P	P
0	0.36	0.41	0.023	0.48	0.36	0.68
50	0.34	0.41	0.020	0.49	0.37	0.67
100	0.34	0.40	0.022	0.43	0.33	0.58
500	0.33	0.40	0.017	0.48	0.29	0.47

*Weighted means for four soils, including data obtained with and without lime.

of Ni on yields when the Ni concentrations reached 60 ppm in oat grain (soil 3, 500 ppm Ni and no lime or P), 28 ppm in oat straw (soil 1, 500 ppm Ni and P), and 44 ppm in alfalfa (soil 3, 50 ppm Ni + lime). The amounts of NH_4OAc-extractable Ni for the corresponding soils and treatments were 9, 29, and 4 ppm. On the other hand, concentrations of Ni as high as 81 ppm in the grain and 33 ppm in the straw (soil 2, 500 ppm Ni and P), and 40 ppm in the alfalfa (soil 3, 50 ppm Ni and lime + P) had no deleterious effect on yield. Corresponding values for NH_4OAc-extractable Ni in the soils were 37 ppm (soil 2) and 3 ppm (soil 3).

DISCUSSION

The beneficial effects of soil organic matter and high pH in reducing extractable Ni in the soils and in maintaining yields of oats, and to a lesser extent alfalfa, at relatively high rates of added Ni are in accord with published data (2, 4, 5). In the work reported herein, these effects were associated also with lower concentrations of Ni in the plants. There is little doubt that management practices including lime and/or organic matter additions are the most effective means of improving production on serpentine and other soils containing high amounts of Ni. The effectiveness of lime in reducing Ni toxicity may be attributed directly to its effect in reducing the level of soluble Ni in the soil (2, 4). Although the effect of lime in maintaining growth (soils 3 and 4) was marked, the pH change was probably not sufficient to provide the maximum benefits possible. The remarkable effectiveness of organic matter in preventing Ni toxicity is undoubtedly due to its ability to form stable complexes with Ni (11, 13), and thus to prevent its uptake by plants.

Although addition of P usually increased soluble Ni in the soils and the Ni content of the plants, there was only one instance where P had a detrimental effect on yield. On the other hand, there were several instances (soils 3 and 4 with low rates of added Ni) where P tended to repress the toxic effect of Ni.

It has been reported by Crooke and Inkson (3) that P increased Ni toxicity in sand cultures and that the adverse effect of P was associated with reduced Fe adsorption. In another study, however, Crooke (2) found that superphosphate added to an acid soil at usual rates had no effect on exchangeable Ni. In a study of reactions of phosphate with exchangeable and soluble Ni, Pratt *et al.* (12) reported that the type of Ni–P compounds formed at pH values $\geqslant 7.0$ should reduce Ni toxicity in soils. In the present study, however, when P and Ni were added to soil 1 (pH 7.0 or above) it would appear that phosphates of Ni were more soluble than other forms such as hydroxides, which are presumed to have been dominant where P was not added (Tables 3 and 5).

The much greater susceptibility of alfalfa than of oats to Ni emphasizes the importance of selecting Ni-tolerant crops when utilizing soils high in Ni. This marked difference in tolerance of crops to Ni has been attributed to differences in the Fe–Ni ratios of the plants, those for alfalfa being low (9). There is evidence that Ni may increase the rate of Fe uptake, but may inhibit its metabolism in the plant (15).

The evidence of a repressive effect of added Ni on growth when the concentrations of Ni reached 60 ppm in the grain and 28 ppm in the straw were in accord with results of others (5, 6). Hunter and Vergnano (6) reported that oats showing a moderate effect of Ni toxicity contained 73 ppm Ni in the grain and 37 ppm in the straw. Subsequently, Hunter (5) working with a Southern Rhodesian soil found that oats showing symptoms of a moderate degree of Ni toxicity contained 32 ppm Ni in the leaves.

The effects of soil properties and treatments on Ni were similar to those reported for Pb, using the same soils and experimental conditions, except that phosphate repressed the solubility of Pb and its uptake by plants (7). However, Ni was more repressive than Pb on plant growth. Pb had little or no effect on the yield of oats although the Pb concentration in the straw was as high as 200 ppm. While both metals repressed alfalfa growth, the effect of added Ni was evident at a rate of no more than 50 ppm. There was no corresponding effect from Pb, however, until it was added at a rate of 10 times this amount.

ACKNOWLEDGEMENTS

The authors gratefully acknowledge the assistance of O. Scott and staff in conducting the pot test, and of I. Duncan and L. Dowser in performing chemical analyses.

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