NICKEL: ITS AVAILABILITY AND REACTIONS IN SOIL

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ABSTRACT

Nickel is an important pollutant element. Nickel content in the range of 50 to 100 mg/g (dry wt. basis) is indicative of its toxicity in plants. The reaction of Ni is dominated by sorption reactions on soil colloids where nature, relative proportions and concentrations are important. The availability of Ni to plants mainly influenced by soil pH. Ni behave largely like Zn in the soil plant system, but it forms strong chelates with soil organic matter, thereby showing closeness to Cu. Nickel is known to have toxic effect on plants. The major uses of Ni to combustion of coals gasoline and oil, alloy manufacture, electroplating and batteries. If the high concentration of Ni is taking up by the human, they cause lung concern.

INTRODUCTION

The discovery of a biological role and essentiality of Ni in plants, animals the concern over the incidental additions of trace metals including Ni to soil in sewage sludge and other wastes (Tiller, 1989) make it important that the behavior of Ni in soils be well understood. The concentration of Ni in soil ranges from 10 to 1000 mg kg^{-1} and in plants is 1 ppm.

Nickel is finding wide use in (1) Combustion of coal (2) In gasoline and oils. (3) In alloy manufacturing (4) In manufacturing of batteries (5) In electroplating and mining.

Some fertilizers and soil amendments, which are used in agricultural, are important source of Ni in soil. Rock phosphate, which is used as a raw material for phosphatic fertilizers, is known to contain Ni ranging between 16.8 to 50.4 mg kg^{-1} and other fertilizers like ammonium nitrate (<0.20 ppm) and Triple super phosphate may also contain 15.6 to 25.2 ppm

Ni (Raven and Loeppert, 1997).

Sources

Igneous rocks are the primary source of the Ni found in soils. In soils the total concentration of a trace element such as Ni is related directly to the concentration in the parent material and to the weathering processes (Mitchell, 1964). The losses of Ni from soil occur in solution either by leaching or in run off, in eroded material and in harvested goods. Gain of Ni to soil occurs naturally through the accession of soil eroded from elsewhere and addition in agricultural chemicals. The concentration of heavy metals (Ni) in some fertilizer & soil amendments given in Table 1.

MATERIALS AND METHODS

B. Solid phase

About 0.001% of the total Ni in a soil is in soil solution at field capacity. Some of the Ni (II) adsorbed

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into the surface both phases may exchange readily with other cations in soil solution or with reagents specifically designed to remove the Ni.
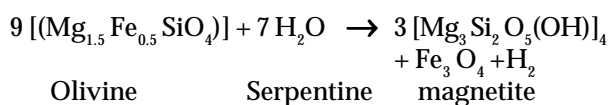
Mitchell (1964) indicated that Ni, in addition to being found in olivine, homablende, augite and biotite, is found in ilmenite and magnetite also. The secondary minerals in the clay fraction that are most likely to accommodate Ni are the hydrous oxides of Fe & Mn and the trioctahedral species of layer silicates the serpentines (1:1), the saponites and vermiculites (2:1) and the chlorites (2:1:1). Concretionary forms of Fe and Mn oxides sometimes have high concentrations of Ni.

The associations of trace metals with the organic matter of the solid phase in soils are considerable significance in determining behavior of soils. The associations of trace metals with the humic and fulvic acids extracted with 0.2 N NaOH from a soil under pasture may be represent forms coordinated in very stable complexes (Table 9).

Reactions

Nickel is a conservative element in the sense that it has the strongest affinity of the common divalent cations for octahedral sites so that is it appears to find itself at home in both layer silicates and hydrous oxides of Fe and Mn.

Yamamoto (1984) found in residues from extracted nonvolcanic ash soils that 30 to 53% of the total Ni (and Zn) was in the residual sand plus silt fraction and 15 to 42% was in the clay fraction. These residual forms have yet to be satisfactorily identified. The process of serpentinization i.e. the formation of serpentine from olivine or related primary minerals can be written.

$$9 \,[(Mg_{1.5}Fe_{0.5}SiO_4)] + 7\,H_2O \longrightarrow 3\,[Mg_3Si_2O_5(OH)]_4 + Fe_3O_4 + H_2$$

Olivine   Serpentine   magnetite

Sorption

The rapid removal of Ni from solution at low concentrations is due to sorption by any of the surfaces proffered by the solid phases of soil. Internal surfaces as well as outer surfaces contribute to the range of surfaces available. The sorption of Ni is strongly pH dependent for hydrous oxides and organic matter, but much less so for illite and kaolinite and virtually absent for montmorillonite (Anderson, 1977). Sorption not only is pH dependent but also on the concentration of suspension, of the Ni itself and of other species of metals and ligands and on time and temperature (Bruemmer *et al.* 1988).

The adsorption studies with mineral soils (Anderson, 1977 & Horter, 1983) show on increasing with increasing pH and for this pH dependency to be more pronounced in A horizons than B horizons, presumably because of the higher organic matter (about 80% O.M.) in A horizons (Harter, 1983).

Mobility

Ni is not completely immobile and that the extent of movement of Ni down through the profile will depends on
a) The forms and quantities applied.
b) The amount of water passing through the profile
c) The soil properties with pH, clay and organic matter content being the most significant, and
d) The properties of the soil to produce soluble organic ligands capable of forming soluble complexes with Ni.
Davis *et al.* 1988 found that the order of mobility on the sandy loam was Cu> Zn> Mo> Cd> Ni> Pb = Cr, whereas on the calcareous loam it was Cu> Mo> Cd = Cu = Pb> Cr = Ni = Zn.

Uptake

The main forms and reactions that are thought to be important in determining the mobility and availability of Ni to plants are illustrated in Fig. 2. Ni^{2+} ion most likely to predominate in the soil solution, to participate in sorption reactions and to be taken up by the plants (Mishra & Kar, 1974; Tinker, 1986).

The soluble forms in the soil solution are the most free to more toward actively absorbing regions of the roots of plants the formation of unchanged and ionic complexes would facilitate diffusion, but at the point of absorption the Ni^{2+} is probably separated from ligands associated with it, in the same way it seems to occur for Cu^{2+} and EDTA (Goodman and Linehan, 1978). Ni^{2+} is actively taken up in much the same way as any divalent metal cation of an essential element such as Zn^{2+} or Mn^{2+}. The site and mechanism of uptake of Ni by barley roots suggests that Ni^{2+} is absorbed actively across the plasma lemma (Korner *et al.* 1986). Cataldo *et al.* (1978) have suggested that uptake of Ni^{2+} occurs in soybeans at the same carrier site as for Cu^{2+} and Zn^{2+}.

Toxicity

The phytotoxic effects of Ni have been known for a long time (Mishra & Kar, 1974). Apart from a decrease

Table 1. Heavy metal concentrations in selected fertilizer and soil amendments (in ppm)

Heavy metal	Rock phosphate (1)	Triple super phosphate (1)	Ammonium nitrate (1)	Dairy manure (mean) (1)	Poultry manure (2)	Swine manure (2)
Arsenic	16.5-20.5	15.3-16.2	<0.40	6.8	-	-
Cadmium	1.3-48.8	5.0-6.2	<0.20	0.7	0.20-0.30	0.50-0.82
Chromium	33.2-140	88.9	-	-	<1.0-7.7	2.2-1.3
Copper	9.6	3.2-3.5	<0.60	18	48-78	250-600
Lead	4.6-29.2	11.1-13.2	<0.40	7.5	6.0-8.4	7.0-11
Mercury	<0.40	<0.40	<0.40	<0.40	-	-
Molybdenum	-	-	-	-	-	-
Nickel	16.8-50.4	15.6-25.2	<0.20	9.6	7.1-9.0	11.33
Selenium	<1.2-2.17	<1.2	-	-	-	-
Zinc	78.8-382	61.3	-	-	330-456	540-1200

(Source: 1. Raven and Loeppert, 1997, 2. Wolfgang and Dohler, 1995)

Table 2. Typical figures and toxic limits for concentrations (ppm) of trace metals in soils and plants

Metals	Soils		Plants	
	Typical	Range	Common range	Toxic limit
Mn	850	100-4000	15-100	500
Co	8	1-40	0.05-0.5	-
Ni	40	10-1000	1.0	25
Cu	20	2-200	4-15	30
Zn	50	10-300	8-15	500

(Source: Leeper (1978)

Table 3. Pollutant elements in cement dust from Nalgonda district

Cement plant	Chromium (ppm)	Nickel (ppm)
Coromendel	200.6	42.6
Hemadri	155.6	37.0
Kakatiya	203.1	41.3
Pamco	133.4	25.1
Mean	173.1	36.5

(Source: Prasad, *et al.* 1985).

Table 4. Analysis of some typic igneous rocks

Trace elements in ppm	Rock type	
	Granite	Basalt
Cd	0.010	0.067
Cr	9.0	16.3
Cu	10.7	22.4
Ni	6.4	18.0
Pb	28.7	18.0
Zn	74.9	132.0

(Source: Flanagan, 1969).

in growth the symptoms of Ni toxicity include chlorosis, stunted root growth and sometimes brown interval necrosis and symptoms specific to the plant

Table 5. Heavy metal composition of coal ash

Elements	Mean coal ash content (ppm)	Crustal abundance (ppm)
Cd	11	0.2
Cr	246	100
Cu	217	55
Mo	60	1.5
Ni	171	75
Pb	287	13
Zn	572	70

(Source: Vine and Tourlets, 1970).

species. The concentrations of Ni associated with Ni toxicity vary widely. For example, Patterns (1971) reported toxicity symptoms in spring wheat at 8 ppm but no yield loss in oats at 90 ppm.

Nickel hyper accumulation

A plant is classified as hyper accumulator when it takes heavy metals against their concentration gradient between the soil solution and cell cytoplasm, and thus acquiring capacity of accumulating a very high metal concentration in tissues without much difficulty in carrying out growth and metabolic functions. Some important Ni hyper accumulators are

Table 6. Heavy metal composition of sewage sludge from different cities in India

City	Cu	Zn	Cd	Cr	Ni	Pb
Ahmedabad	535	2147	3.5	60.4	32.3	76.8
Delhi	440	1610	5.5	53.5	815	34.5
Nagpur	272	832	1.5	49.2	14.8	24.3
Channai	210	935	8.3	38.5	60.5	16.6
Jaipur	39.1	1720	7.3	176	37.5	66.9

(Source : Maiti, *et al.*1992).

Table 7. Values of maximum allowable limits for heavy metals in different countries (mg kg^{-1})

Element	Austria	Canada	Poland	Japan	Great Britain	Germany
Cd	5	8	3	-	3	2
Co	50	25	50	50	-	-
Cr	100	75	100	-	50	200
Cu	100	100	100	125	100	50
Ni	100	100	100	100	50	100
Pb	100	200	100	400	100	500
Zn	300	400	300	250	300	300

(Source: Rattan, *et al.* 2002).

Table 8. Concentration (ppm) of Ni, Cu, Co and Mn in the constituent minerals of a Hypersthene olivine Gabbro

Metals	Constituent minerals				
	Plagioclase	Pyroxene	Olivine	Total from minerals	Found in rocks
Ni	<2	150	350	120	135
Co	<2	50	125	40	55
Cu	40	35	20	35	80
Mn	<10	2100	1700	940	700

(Source : Mitchell, 1964).

Table 9. Co, Cu, Mn and Ni associated with humic and fulvic acids extracted with 0.2 N NaOH from a soil under pasture

Fraction	Organic matter		Co		Cu		Mn		Ni	
	ppm	(%)	ppm	%	ppm	%	ppm	%	ppm	%
Whole soil	123	100	47	100	28	100	2200	100	35	100
Humic acid	18.2	15	0.66	1.4	1.9	6.8	4.3	0.2	0.59	1.7
Fulvic acid	54.3	44	0.73	1.6	2.4	8.6	23.8	1.1	0.57	1.6

(Source: Cheshive *et al.,* 1977)

given below.

1. *Brassica juncea* (mustard)
2. *Streptanthus polygaloides* Gray (Brassicaceae)
3. *Silene spp.* (Cryophyllaceae) – *S. vulganis, S. burchelli, S. cobaltica, S. nflata, S. diocia* – These varieties of *silene* is produced highest dry matter yield and also remediate > 10000 ppm Ni from the polluted soils.
4. *Thlaspi spp.* (Brassicaceae) - *T. cacrulescens, T. montanum, T. ochlecum.*
5. *Alyssum spp.* (Brassicaceae) - *A. argentum, A. corsicum, A. euboeum, A. heldrechii, A. murale, A. cnium, A. troodii* (Baker *et al.* 2000)

Bioaccumulation coefficient is a useful indicator of hyper accumulating efficiency of plant (Table 13)

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Table 10. Concentrations of Ni, Mn and Zn in a serpentine soil

| Elements | Original | Clay | Fine sand | | | Coarse sand | | |
| | | | | Nonmagnetic | | | Nonmagnetic | |
			Magnetic	Heavy	Light	Magnetic	Heavy	Light
Ni	2600	2500	1370	760	1700	1000	817	1960
Mn	1080	500	4030	2730	500	2700	2900	370
Zn	170	280	1610	456	180	318	259	114
Proportion (%)								
Whole soil	100	33.7	0.20	1.28	11.3	0.60	0.17	6.72
Total Ni	100	32.4	0.1	0.4	7.4	0.2	0.05	5.1

(Source: Suzuki *et al.,* 1971)

Table 11. Effect of P and rates of Ni and Zn on yield, concentration and uptake of Ni and Zn in corn grown on Grenville loam.

| Rate of metals added (mg/g) | P added (mg/g) | Mean yield (g/pot) | | Mean concentration (mg/g) | | Mean uptake (mg/pot) | |
		Ni	Zn	Ni	Zn	Ni	Zn
0	0	5.6	5.6	0.6	48	3.4	269
60	0	3.8	4.7	1.6	146	6.1	686
240	0	2.0	5.7	21.9	397	43.8	2263
480	0	0.5	5.7	78.1	709	39.1	4041
0	50	12.7	12.7	0.6	28	7.6	356
60	50	9.9	12.2	1.5	60	14.9	732
240	50	2.4	11.5	17.6	292	42.2	3358
480	50	0.3	10.0	166.1	432	49.8	4360

(Source: Maclean & Dakker, 1978).

Table 12. The effect of pH and Ni additions on the concentration (ppm) of Ni in spring wheat

| Soil pH | Ni added to soil (ppm) | | | | | | |
	0	5	10	20	40	80	160
5.1	2.5	4.5	3.0	8.0	10.0	74.0	-
5.5	2.2	2.5	3.7	4.7	6.5	17.2	105.0
6.5	1.0	0.75	2.2	2.0	2.75	3.0	8.25
7.5	-	0.5	0.5	-	0.75	1.25	3.0

(Source: Patterson, 1971).

Table 13. Bioaccumulation coefficients of various *Brassica* species at maturity stage

| Species | Heavy metals (mg kg^{-1}) | | | |
	Zn	Cu	Ni	Pb
B. juncea	6.83	3.08	3.21	12.86
B. compestris	12.48	2.59	13.61	2.56
B. carinata	11.89	1.94	12.30	17.72
B. napus	9.87	1.14	8.98	9.37
B. nigra	6.56	2.04	8.66	7.94

(Source: Bhadrawaj *et al.* 2004)

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