Influence of Soil Moisture Regimes, Amendments and Ageing on Nickel Availability in Soils

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In a range of nickel (Ni) spiked soils the effects of soil moisture regimes, amendments and ageing on Ni availability were estimated. The soil was spiked with Ni @ 0, 10 and 25 mg kg^{-1} soil through its nitrate solution. Lime (5%), farmyard manure (20 t FYM ha^{-1}) and zinc (25 mg Zn kg^{-1}) were added. The treated soil samples were incubated at 35 °C for 1, 45 and 90 days at field capacity and submerged soil moisture regimes. Available Ni was extracted with 0.005 M DTPA extractant and determined by ICP-AES. The results revealed that there was a temporal decrease in the available Ni with ageing and was in the order of 1 day > 45 days > 90 days. The magnitude of decrease in Ni availability was higher with the addition of amendments in the order of lime > FYM > Zn > unamended soil. The decrease in available Ni was further pronounced under submerged moisture regime than under field capacity. The mean per cent recovery of DTPA-Ni in the 10 mg Ni kg^{-1} spiked treatment decreased from 57.6 after 1 day of incubation to 29.3 and 26.8 after 45 and 90 days of incubation, respectively; whereas in the 25 mg Ni kg^{-1} spiked soil, per cent recovery of Ni decreased from 60.0 after 1 day of incubation to 29.0 and 25.1 after 45 and 90 days of incubation, respectively. An overall reduction in the mean per cent recovery of DTPA-Ni was observed under submergence as compared to field capacity moisture regime in lime, FYM, Zn amended soils and unamended soil. The results enable us to understand the effect of ageing coupled with different amendments under various moisture regimes on Ni availability and provide useful information to work out the capacity of the soil to serve as a sink for Ni.

Key words: Nickel, availability, spiking, amendments, moisture regimes, ageing

Heavy metal contamination in soil occurs either due to toxic metals from groundwater or through various anthropogenic activities. Heavy metals such as manganese (Mn), iron (Fe), copper (Cu) and zinc (Zn) are essential for plants, animals and microorganisms, while cadmium (Cd), lead (Pb), nickel (Ni), chromium (Cr) and mercury (Hg) have no known biological or physiological functions but are toxic to soil-plant-animal-human continuum (Alloway 2012; Bolan *et al.* 2014). Diagnosis of the effects of metal toxicity is often non-specific which slowly accumulate in the body, thereby, affects human health without producing specific clinical symptoms (WHO 1993). Nickel is the third most widespread heavy metal after Cd and Pb, and is listed as one of essential micronutrient elements for plant growth and development (Liu 2001; Bai *et al.* 2006). Plants require Ni only at <0.5 mg kg^{-1} of dry weight, but when its concentration increases beyond a critical level, it leads to chlorosis of leaves, stunting of roots and deformation of various plant organs (Marschner 2012). Although its concentration in soil usually remains below 50 mg kg^{-1} (McGrath 1995), Ni could be hazardous depending on its potential availability in soils. Bioavailability of Ni can be minimized through chemical and biological immobilization using a range of inorganic compounds such as lime, phosphate compounds (*e.g.*, rock phosphate) and organic materials such as farmyard manure (FYM), press mud and poultry manure (Bolan *et al.* 2014; Shahid *et al.* 2014; Kalsi *et al.* 2016). The immobilization and consequent reduction in availability of Ni could be achieved through formation of organic and inorganic metal complexes, precipitation and subsequently, its reduction to immobile forms (Parida *et al.* 2003; Shaheen *et al.* 2019).

Mobility and bioavailability of Ni can be reduced through its reaction with soil for a longer period, or through addition of amendments (Park *et al.* 2011). With ageing, Ni availability may decrease

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due to micropore diffusion, cavity entrapment, occlusion in minerals and organic constituents by co-precipitation and co-flocculation, and surface precipitation (Settimio *et al.* 2014). The above reactions are affected by soil pH, cation exchange capacity (CEC), clay content, soil texture, and total and dissolved soil organic matter (Guo *et al.* 2011; Antoniadis and Alloway 2012). Soil moisture regime affects pH, redox potential (Eh), organic matter and $CaCO_3$ contents of soil (Van den Berg and Loch 2000), and therefore may influence Ni availability.

It is important to investigate the process of Ni spiking with reference to ageing on available fraction which is directly related to the management and prevention of soil contamination. However, most of the investigations have been performed with unamended soils. Amending soil with different organic or inorganic substances such as manures, lime, composts, plant residues and nutrient elements may help to decrease metal availability (Kalsi *et al.* 2016). Metal availability in soil also decreases with time after the contamination (Lu *et al.* 2005). A laboratory experiment was planned to investigate the ageing phenomenon with addition of amendments under various soil moisture regimes over a range of Ni contamination.

Materials and Methods

Uncontaminated surface (0–15 cm) soil was collected from a cultivated field in the experimental farm of Punjab Agricultural University, Ludhiana, India. The soil was air-dried, ground to pass through a 2-mm sieve, homogenized and then put in 100 mL plastic vials. The soil belongs to Ustipsamments, sandy loam in texture having pH 7.87, organic carbon 3.9 g kg^{-1}, DTPA-Ni 0.12 mg kg^{-1} with 19.2% field capacity. Soil sample (30 g) was taken in vials, and each vial was spiked artificially with 0, 10 and 25 mg Ni kg^{-1} through nickel nitrate hexahydrate [$Ni(NO_3)_2.6H_2O$]. The spiking levels were representative of the range of contamination levels (safe limit: 10 mg kg^{-1}) found in polluted sites (Sikka *et al.* 2009). The spiked soil samples in separate vials were further amended with $CaCO_3$ (5%), FYM (20 t ha^{-1}) and Zn (25 mg kg^{-1}). The treated soil samples were incubated at two moisture regimes *viz.*, field capacity and submergence at 35±1 °C for 90 days with 3 replications. The incubation temperature corresponds to prevalent temperature in basmati rice growing season. In submergence, soil surface in vial was marked and water was added till it was standing 1 cm above the surface. In field capacity, soil samples

were weighed every alternate day and the loss in moisture was compensated by adding water to keep the soil moisture constant. During ageing, the soil was mixed once a week with a laboratory spoon. Whole of the soil sample was extracted with 0.005 *M* DTPA (Lindsay and Norwell 1978) for Ni on 1, 45 and 90 days after spiking. The moisture content of soil samples of both the moisture regimes was taken care for measuring concentrations of various metals to present the data on oven dry basis. The metal concentrations were determined using ICP-AES (Inductively coupled plasma - atomic emission spectrometer, Thermo 6300) with detection limit of ppb.

Results and Discussion

Although no significant changes were observed after 1 day in control (0 mg kg^{-1}), the DTPA-Ni decreased from 0.14 mg Ni kg^{-1} soil with no amendment to 0.08 mg Ni kg^{-1} soil with the addition of both lime and FYM after 45 days of incubation (Table 1). However, no change was recorded with addition of Zn. Similar observations were recorded under submergence moisture regime. After 90 days of incubation, similar changes were observed under both the soil moisture regimes. At 10 mg Ni kg^{-1} and after 1 day of incubation, DTPA-Ni decreased from 5.95 mg kg^{-1} with no amendment to 5.60 with addition of lime only under field capacity moisture content; however, the decrease was significant with all amendments under the submerged condition (from 6.1 to 5.61, 5.76 and 5.3 mg kg^{-1} with addition of lime, FYM and Zn, respectively). After 45 and 90 days of incubation, DTPA-extractable Ni decreased substantially with both FYM and lime, although with Zn treatment, changes were non-significant. Results were similar under field capacity and submergence regimes. It was observed that DTPA-Ni content substantially decreased to 3.78 mg kg^{-1} from 5.95 mg kg^{-1} under unamended soil under field capacity which further reduced significantly to 2.8 and 2.4 mg kg^{-1} with addition of FYM and lime, respectively and under submerged moisture regime it further decreased to 2.2 and 1.88 mg kg^{-1}, respectively.

With 10 mg Ni kg^{-1} soil, the mean values of DTPA-Ni irrespective of the amendments were 5.82, 3.20 and 2.75 mg kg^{-1} soil at 1, 45 and 90 days after incubation, respectively under field capacity, whereas the respective values in submerged moisture regime were 5.69, 2.67 and 2.61 mg kg^{-1} soil. The reduction in DTPA-Ni was larger with further spiking. At 25 mg Ni kg^{-1} of soil, DTPA-Ni decreased marginally

Table 1. Available Ni as influenced by Ni spiking, amendments, ageing and moisture regimes

Amendments	Days after incubation (DAI)								
	1 day			45 days			90 days		
	FC[#]	SB	Mean	FC	SB	Mean	FC	SB	Mean
0 mg Ni kg⁻¹									
Control	0.14	0.13	0.13	0.14	0.12	0.13	0.14	0.12	0.13
Lime	0.12	0.12	0.12	0.08	0.07	0.07	0.08	0.04	0.16
FYM	0.16	0.12	0.14	0.08	0.08	0.08	0.10	0.08	0.09
Zn	0.13	0.13	0.13	0.13	0.12	0.12	0.14	0.13	0.13
Mean	0.14	0.12		0.11	0.10		0.11	0.09	
LSD (P=0.05)	NS	NS		0.03	0.02		0.03	0.02	
10 mg Ni kg⁻¹									
Control	5.95	6.10	6.03	3.78	3.28	3.53	3.28	3.18	3.23
Lime	5.60	5.61	5.60	2.40	1.88	2.14	2.10	1.78	1.94
FYM	5.88	5.76	5.82	2.80	2.20	2.50	2.40	1.98	2.19
Zn	5.84	5.30	5.57	3.80	3.30	3.55	3.20	3.48	3.34
Mean	5.82	5.69		3.20	2.67		2.75	2.61	
LSD (P=0.05)	0.18	0.35		0.12	0.09		0.11	0.13	
25 mg Ni kg⁻¹									
Control	15.9	15.5	15.7	9.62	8.13	8.87	8.73	7.83	8.33
Lime	14.8	14.1	14.4	5.90	5.12	5.51	4.32	4.12	4.22
FYM	14.7	13.5	14.1	6.44	5.80	6.12	4.90	4.54	4.72
Zn	15.7	15.8	15.7	9.10	8.02	8.56	7.82	8.14	7.98
Mean	15.3	14.7		7.77	6.77		6.44	6.16	
LSD (P=0.05)	NS	NS		0.89	0.76		0.81	0.54	

[#]FC - Field capacity; SB - Submergence

after 1 day of incubation. However, decrease was significant with FYM and lime, but not with addition of Zn under both the moisture regimes. At 90 days incubation, significant decrease in DTPA-Ni was observed with all amendments under the field capacity moisture regime, but only with lime and FYM under submerged soil condition. In the 25 mg Ni kg⁻¹ spiked soil under field capacity, the mean values of DTPA-Ni irrespective of the amendments were 15.3, 7.77 and 6.44 mg kg⁻¹ soil at 1, 45 and 90 days after incubation, respectively, whereas the respective values in submerged regime were 14.7, 6.77 and 6.16 mg Ni kg⁻¹ soil.

The results indicated that the contamination level of Ni and aging had a significant influence on curtailing the bioavailability of Ni as determined by DTPA-extractable Ni (Table 1) among all amendments and moisture regimes. Liu *et al.* (2015) reported that there was no adverse effect of the long-term field aging on Ni toxicity to *Folsomia candida,* rather there was a significant decrease in the availability of Ni. It was also suggested that field aging should be taken into account on toxicity testing and risk assessment practices. Ma *et al.* (2017) also reported that with aging the exchangeable Ni in soils decreased sharply

initially followed by a slower decrease during later stage. The initial fast process was attributed to precipitation followed by micropore diffusion process.

After 1 day of incubation in 10 mg Ni kg⁻¹ spiked soil, mean per cent recovery of DTPA-Ni was similar with and without amendments under field capacity (Table 2). However, after 45 days of incubation, the changes were significant which recorded 37.8% in control and 24.0 and 28.0% with addition of lime and FYM, respectively. After 90 days of incubation, the Ni recovery further decreased from 32.8% in control to 21.0 and 24.0% with addition of lime and FYM, respectively. Similar observations were recorded under submerged moisture regime also. Irrespective of amendments and moisture regimes in the 10 mg Ni kg⁻¹ spiking, the mean recovery of DTPA-Ni was 57.6, 29.3 and 26.8%, respectively at 1, 45 and 90 days of incubation. In 25 mg Ni kg⁻¹ spiking, the respective recovery was 60.0, 29.0 and 25.1%. The data clearly indicated that the magnitude of decrease in DTPA-Ni extraction was much higher from 1 to 45 days as compared to decrease in DTPA-Ni recorded from 45 to 90 days where only a meager decrease from 29.3 to 26.8 and from 29.0 to 25.1% occurred at 10 and 25 mg Ni kg⁻¹ spiking, respectively.

Table 2. Per cent recovery of Ni as influenced by Ni spiking, amendments, incubation period and moisture regimes

Amendments	Days after incubation (DAI)								
	1 Day			45 days			90 days		
	FC	SB	Mean	FC	SB	Mean	FC	SB	Mean
10 mg Ni kg⁻¹									
Control	59.5	61.0	60.3	37.8	32.8	35.3	32.8	31.8	32.3
Lime	56.0	56.1	56.0	24.0	18.8	21.4	21.0	17.8	19.4
FYM	58.8	57.6	58.2	28.0	22.0	25.0	24.0	19.8	21.9
Zn	58.4	53.0	55.7	38.0	33.0	35.5	32.0	34.8	33.4
Mean	58.2	56.9	57.6	31.9	26.7	29.3	27.5	26.1	26.8
LSD (P=0.05)	NS	2.68		2.84	2.35		2.18	3.62	
25 mg Ni kg⁻¹									
Control	63.6	62.1	62.9	38.4	32.4	35.4	34.9	31.3	33.1
Lime	59.2	56.2	57.7	23.6	20.4	22.0	17.2	16.4	16.8
FYM	58.8	54.0	56.3	25.6	23.2	24.4	19.6	18.0	18.8
Zn	62.9	63.2	63.1	36.4	32.0	34.3	31.2	32.4	31.8
Mean	61.1	58.9	60.0	31.0	27.0	29.0	25.7	24.5	25.1
LSD (P=0.05)	NS	2.86		3.27	3.18		3.64	3.47	

#FC- Field capacity; SB - Submergence

Results suggest that during initial 45 days of addition of amendments, maximum reductions in per cent extractability of added metal happened and thereafter a quasi-equilibrium was reached. Further increase in aging or reactivity resulted in a marginal decrease in the per cent extractability of the metal. Similarly, when the mean per cent extractability of DTPA-Ni irrespective of incubation period was compared, highest extraction (61.0%) in 10 mg Ni kg⁻¹ spiking was recorded with non-amended soil under submergence, moisture regime whereas lowest per cent extractability was observed under soils treated with lime and kept under submergence (17.8%). Shehnaz *et al.* (2019) also reported that the addition of lime and FYM resulted in significant decrease of water soluble and exchangeable fractions of Ni which are considered to be available fractions. Earlier in another study Justyna and Maria (2013) reported that Ni solubility declined with the addition of Zn, Cu and aging. But the decline was more pronounced with aging compared to addition of Zn and Cu.

The period of contact of Ni with soil and addition of lime (CaCO₃) and FYM as amendments are important factors that controlled the Ni availability. The decrease in availability of Ni with addition of lime may be attributed to the stronger binding of Ni with CaCO₃, its precipitation by CaCO₃ and possible rise in pH of the soils by the addition of lime (Kansal *et al.* 1996). Rapid decrease in extractable Ni with increase in incubation period indicated that Ni takes time to react with the soil and in 45 days of incubation, more than 60% of it transformed into unavailable forms.

In unspiked soil (0 mg Ni kg⁻¹ soil), FYM contributed 0.12 mg Ni kg⁻¹, but at higher levels of spiking, the organic constituents and the DTPA might be competing for Ni, and the decrease in metal extraction would be a net effect of these two factors. The decrease in DTPA-Ni with addition of FYM might be due to formation of stable organo-metal constituents. Aziz *et al.* (2016) observed that FYM forms multidentate complexes which immobilize heavy metals such as Pb, Cd and Ni in soils. Deka *et al.* (1997) reported that FYM influenced the sorption of metals in soil through complexation on the surface of solid organic matter, precipitation of hydroxides of metals and formation of stable organo-metal complexes. In the first case, there was an increase, while for the others, there was decrease in the availability of metals in soil. In the present study, formation of precipitable Ni hydroxides and/or stable organo-metal complexes might seem most likely, resulting in a decrease in extraction of Ni in FYM treated soils. Solution pH regulates the protonation and deprotonation of inorganic and organic -COOH groups, thereby affecting the surface charge and the number of available sites in soils, minerals or organics for sorption of Ni or other specific sorbing ions. The ability of soils to sorb a metal has been found to be inversely related to the extent of extraction and availability of metals (Adriano 2001). The redox potential (Eh) decreases both with the addition of organic matter and with submergence. With decrease in Eh under submergence, the solubility of Fe and Mn increases by reductive dissolution process (Kashem and Singh 2001). Hydrous Mn and Fe oxides are

thought to immobilize heavy metals by providing sites for their sorption in most soils. Moreover, under submergence, sulphate ions are reduced to sulphide that may form complex with Ni and immobilize them as sulphide salts. Effects of Eh and pH on metal solubility although depends on metal type in soil, the solubility of Ni decreased with increase in the duration of flooding. All of the above stated reasons might also be responsible for the decrease in Ni availability in the present study.

Conclusions

From the results of the present study it may be concluded that ageing and addition of amendments have desirable effects of reducing Ni availability and more so under submerged soil moisture regime and thus may prevent Ni toxicity. Both at lower and higher levels of Ni spiking along with addition of 5% lime resulted in the least recovery of spiked Ni. Therefore, addition of lime may be a viable alternative to stabilize soil highly contaminated with Ni. Although the results may provide some insight into Ni availability mechanism with the addition of different amendments but the inter-correlations of diverse soil characteristics may lead to inaccurate conclusions. Nonetheless, these provide useful information to work out the capacity of the soil to serve as a sink for metals.

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