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Irappa N Nagara
 Department of Soil Science and
 Agricultural Chemistry, College
 of Horticulture, Bagalkot,
 Karnataka, India

Effect of various ameliorants on immobilization and bioavailability of nickel in spiked soils

Irappa N Nagara

Abstract

Nickel (Ni) is just one of a variety of ubiquitous trace metals emitted into the environment from both natural and anthropogenic sources. Immobilization of such toxic metal in soil using ameliorants is a cost-effective technique for heavy metal contaminated soils. Hence, this study aimed to determine the efficacy of different ameliorants to immobilize nickel (Ni) in spiked soils and thereby reduce their bioavailability. An incubation experiment was established with nickel spiked soil. Such soil was treated with different ameliorants such as lime (CaCO_3), potassium di-hydrogen phosphate (KH_2PO_4), biochar, FYM, vermicompost, zeolites (clinoptilolites), gypsum and pressmud. Phyto-available nickel was evaluated through selective sequential extraction. There observed a significant reduction in mobile Ni after addition of the amendments. The lime, pressmud, vermicompost and zeolite have high potential in reducing mobile pool of Ni at different incubation intervals.

Keywords: Spiked soil, immobilization, ameliorants, remediation

Introduction

Contamination of agricultural soils by potentially hazardous metal (Ni) disturbs ecosystem and threatens food safety. Mobility of such toxic metal contaminates the soil and groundwater thereby increasing the possibility of entering into the food chain via phytotoxicity and reaching human body (Taghipour *et al.*, 2013) [11]. Emsley (1991) [3] reported that nickel decreases the uptake of macro and micro nutrients on the competition for common binding sites due to comparable ionic radii of nickel and other cations. Thus, remediation of such heavy metals in contaminated soils has received an increasing attention and issue for environmental management. *In-situ* immobilization technique is promising because of its easy availability, effectiveness and low cost (Shaheen *et al.*, 2015) [7]. A strategy commonly used to study the mobility of metals agricultural soils is to use selective sequential extraction procedures such as those developed by Kashem and Sing (2001) [5] or Tessier *et al.* (1979) [12] or Shuman (1985) [9]. The procedures, with the use of extractant to estimate the metal distribution among the water soluble, exchangeable, carbonate, oxide, organic and residual fractions.

This study was conducted in short term pot experiment with an objective of reducing mobile pool of nickel and to assess the effectiveness of different ameliorants on reducing the phytoavailable fractions of nickel in spiked soils.

Material and Methods

Soil: Soil vulnerable for nickel contamination with slightly acidic soil pH and low soil organic carbon were used for remediation studies. Initial soil properties are depicted in Table 1.

Table 1: Salient soil properties for remediation study

Parameters	Values
pH (Soil: water, 1: 2.5)	6.5
EC (Soil: water, 1: 2.5) (mS m^{-1})	0.17
Organic carbon (%)	0.1
Available N (kg ha^{-1})	223.6
Available P_2O_5 (kg ha^{-1})	28
Available K_2O (kg ha^{-1})	216
Available S (kg ha^{-1})	24
Available Ca ($\text{meq} / 100\text{g}$)	24
Available Mg ($\text{meq} / 100\text{g}$)	16.2
Free CaCO_3 (%)	4.2
DTPA extractable Fe, Mn, Zn and Cu (mg kg^{-1})	1.42, 4.45, 0.3 and 0.1 ppm

Corresponding Author:
Irappa N Nagara
 Department of Soil Science and
 Agricultural Chemistry, College
 of Horticulture, Bagalkot,
 Karnataka, India

Metal spiking and incubation

Nickel nitrate was spiked to a vulnerable soil to induce the contaminated condition. A critical concentration of 100 ppm of $\text{Ni}(\text{NO}_3)_2$ was maintained in each kg soil samples. Eight ameliorants *i.e.* lime (AR grade), potassium di-hydrogen orthophosphate (KH_2PO_4 AR grade), biochar, FYM, vermicompost, zeolite, gypsum and pressmud were blended with soil separately at 1.0, 1.0, 5.0, 10, 2.0, 1.0, 1.0, 3.0% (w/w) respectively. Absolute control with no amendment was also maintained simultaneously. Each treatment was repeated thrice and the moisture content near to field capacity was maintained so as to facilitate amelioration process. Soils spiked with Ni and ameliorates were incubated at room temperature for 60 days. Sub-sample soils from each treatment were taken after 20, 40 and 60 days of incubation and subjected to sequential extractions with the protocol developed by Kashem and Singh (2001)^[5].

Ameliorants

Eight ameliorants such as lime, potassium di-hydrogen orthophosphate (KH_2PO_4 AR grade), biochar, FYM, vermicompost, zeolite, gypsum and pressmud were chosen for the remediation study based on the cost feasibility and easy availability. The lime with pH of 8-9 (calcium carbonate equivalent of 100). The Potassium di-hydrogen orthophosphate (KH_2PO_4), AR reagent was used as soluble (P) source to immobilize heavy metals which act as buffering agent. Rice husk biochar (RHB) with pH (7.7), electrical conductivity (EC) 3.4 mS m^{-1} , TOC 39 percent. FYM with soil reaction (7.9), electrical conductivity (EC) 0.6 mS m^{-1} , Total organic carbon (TOC) 27%. The vermicompost with pH (7.7), electrical conductivity (EC) 1.1 mS m^{-1} , TOC 21%. The zeolites (0.5-2.0 mm) with a CEC of 120 $\text{cmol}(\text{p}^+)\text{kg}^{-1}$, composed by oxides of Si (68.3%), Al (13%), Ca (2%), Fe (1.4%), K (4%) was obtained from Escott Zeolites Inc., Australia. Further, it helps in controlling the soil reaction and gypsum containing neutralizing value is 0.6 were used in this study.

Sequential extraction procedure

Two grams of spiked soil was taken in centrifuge tube and the following the sequential extraction procedure. The different fractions of Cd, Ni and Pb were extracted using 20 mL distilled water for 1 h (water soluble), 20 mL of 1M ammonium acetate at soil reaction of 7 for 2 h (exchangeable), 20 mL of 1M ammonium acetate at soil pH of 5 for 2 h (carbonate bound), 20 mL 0.04 M hydroxylamine hydrochloride in 25% acetic acid (v/v) at pH for 6 h in a water bath at 80 °C with occasional shaking (oxide bound), then 15 mL of 30% H_2O_2 at pH 2 for 5.5 h in water bath at 80 °C with occasional shaking, followed by centrifuge with 5 mL of 3.2 M ammonium acetate in 20% (v/v) HNO_3 for 0.5 h (organically bound) and finally 20 mL 7 M HNO_3 for 6 h in a water bath at 80 °C with occasional shaking (residual fraction). After extraction, different forms of Cd, Ni and Pb were determined by Microwave plasma atomic emission spectroscopy (MP-AES). The soil pH (1:1 soil water extract) was also determined for each sample.

Results and Discussion

At 20 days of incubation interval (Ni fractions)

The Ni retention in control followed the order of oxide bound > residual > organic bound > carbonate > exchangeable > water soluble. However, the distribution of Ni in various fractions followed a different trend in soils treated with various ameliorants. All the ameliorants significantly reduced the phytoavailable fractions of Ni compared to that of control (14.01%). Among the different treatments involving various ameliorants, one percent lime recorded the lowest (5.12%) phytoavailable Ni owing to near neutral pH. Remediation efficacy of various ameliorants existed in the sequence of lime > KH_2PO_4 , zeolite > gypsum > pressmud > biochar > vermicompost > FYM > control (Table 8). Percentage reduction of mobile Ni at this interval was found superior in zeolite (76.4%) compared to control among the amendments used (Table 1)

At 40 days of incubation interval (Ni fractions)

With the lapse of time, the retention by exchangeable fraction exceeded that of carbonate form. This sequence varied significantly with amendment addition. The maximum phytoavailable Ni (11.99%) was observed in control where the soil did not receive any amendment (Table 2). Among the different ameliorants, the three percent pressmud significantly reduced the phyto-available Ni (2.20%) with neutral pH which was found to be the lowest among the ameliorants. Upon incubation the overall rating of ameliorants efficacy in immobilization of Ni was in the order of pressmud > lime > vermicompost > FYM > KH_2PO_4 > zeolite > gypsum > biochar > control. Percentage reduction of mobile Ni at this interval was found superior in lime (88.5%) compared to control among the amendments used.

At 60 days of incubation interval (Ni fractions)

At this incubation interval the pH (5.8) was found to be the lowest among the intervals and treatments. Further, maximum mobile pool of Ni (9.7%) was observed in control soils compared to ameliorant treated soils. The sequence of Ni distribution altered with ameliorant addition. Among the ameliorants treated soils, three percent pressmud showed the lowest phyto-available (1.66%) Ni. With lapse of incubation time, the remediation efficacy of ameliorants followed the order of pressmud > vermicompost > FYM > KH_2PO_4 > lime > zeolite > gypsum > biochar > control. Over the period of incubation the mobile pool of Ni was significantly reduced by pressmud compared to other treatments as well as prior short term intervals. Percentage reduction of mobile Ni at this interval was found superior in vermicompost (90.4%) compared to control among the amendments used. Organic matter (pressmud and vermicompost) controls the bioavailability of Ni in contaminated soil due to formation of stable chelates, which controls the accumulation and mobility of Ni in the soil as indicated by Stevenson and Cole (1999)^[10]. Further, it may be due to by-products released during OM decomposition, changes in redox potential and protonation/deprotonation (Hamid *et al.*, 2019)^[4].

Vermicompost is used as a bio-sorbent for removing metallic ions such as Pb, Ni, Cd and Cr from wastewaters since it has maximum adsorption capacity for heavy metals (Mudhoo *et al.*, 2012; Zhu *et al.*, 2017) [6, 13].

The addition of lime to heavy metal contaminated soils is well known strategy to increase soil pH, induces precipitation of metal carbonates, oxides or hydroxides and decreases the

solubility of heavy metal (Chlopecka and Adriano 1996; Castaldi *et al.*, 2005b) [2, 1].

Zeolites promotes the adsorption of Ni on its surface and induces precipitation of Ni with its oxides thereby causing effective immobilization and reducing labile Ni as reported by Shi *et al.* (2009) [8]

Table 1: Sequential extraction of Ni spiked soil at 20 days of incubation period treated with different ameliorants

Treatment	Water soluble	Exchange-able	Carbonate bound	Oxide bound	Organic bound	Residual	Total Ni (mg kg ⁻¹)	Mobile Pool of Ni (%)	Reduction (%) Mobile Ni	pH(1:1)
1% Lime	0.02 ^d	0.06 ^g	1.63 ^d	14.29 ^c	4.73 ^c	12.66 ^{cd}	33.39 ^c	5.12 ^h	73.5	7.4
1% KH ₂ PO ₄	0.02 ^d	0.12 ^f	1.43 ^e	11.03 ^f	3.65 ^e	13.64 ^b	29.89 ^f	5.25 ^g	75.7	6.8
5% Biochar	0.03 ^c	0.29 ^b	1.46 ^e	9.93 ^g	3.65 ^e	12.97 ^c	28.33 ^h	6.17 ^d	72.4	6.5
10% FYM	0.01 ^e	0.22 ^c	2.23 ^b	11.78 ^e	3.59 ^e	15.17 ^a	33.00 ^d	7.45 ^b	61.8	6.9
2% Vermicompost	0.01 ^e	0.18 ^d	1.86 ^c	11.57 ^e	4.85 ^{bc}	12.68 ^{cd}	31.16 ^e	6.58 ^c	68.2	6.5
1% Zeolite	0.02 ^d	0.15 ^e	1.35 ^f	12.33 ^d	4.14 ^d	10.93 ^e	28.92 ^g	5.26 ^g	76.4	6.6
1% Gypsum	0.04 ^b	0.16 ^e	1.83 ^c	16.03 ^b	5.07 ^b	13.47 ^b	36.60 ^b	5.55 ^f	68.4	7.2
3% Pressmud	0.02 ^d	0.13 ^f	1.45 ^e	10.00 ^g	4.07 ^d	12.26 ^d	27.93 ⁱ	5.73 ^e	75.2	6.6
Control	0.16 ^a	1.41 ^a	4.88 ^a	19.93 ^a	6.93 ^a	12.74 ^c	46.05 ^a	14.01 ^a		6.3
C.D.(P=0.05)	0.003	0.01	0.05	0.54	0.26	0.44	0.05	0.03		0.1
SE(m) ±	0.00	0.00	0.02	0.18	0.09	0.15	0.02	0.01		0.0
SE(d)	0.0	0.01	0.02	0.26	0.12	0.21	0.02	0.02		0.1
C.V.	4.72	2.21	1.35	2.42	3.34	1.94	0.09	0.29		1.2

Table 2: Sequential extraction of Ni spiked soil at 40 days of incubation period treated with different ameliorants

Treatment	Water soluble	Exchange-able	Carbonate bound	Oxide bound	Organic bound	Residual	Total Ni (mg kg ⁻¹)	Mobile Pool of Ni (%)	Reduction (%) Mobile Ni	pH(1:1)
1% Lime	0.00	0.08 ^g	0.60 ^d	11.92 ^d	5.57 ^{ef}	11.10 ^c	29.28 ^f	2.32 ^h	88.5	7.8
1% KH ₂ PO ₄	0.03 ^d	0.43 ^d	0.59 ^d	11.77 ^{de}	6.93 ^c	13.88 ^a	33.62 ^d	3.12 ^e	82.3	7.4
5% Biochar	0.02 ^e	0.65 ^b	0.63 ^c	11.30 ^{ef}	5.92 ^d	8.97 ^d	27.49 ^h	4.73 ^b	78.0	7.0
10% FYM	0.01 ^g	0.33 ^f	0.47 ^e	11.00 ^f	5.74 ^{de}	10.60 ^c	28.14 ^g	2.88 ^f	86.3	7.3
2% Vermicompost	0.01 ^g	0.49 ^c	0.33 ^h	12.96 ^c	4.63 ^g	10.93 ^c	29.36 ^e	2.83 ^g	85.9	7.2
1% Zeolite	0.01 ^g	0.64 ^b	0.45 ^f	12.00 ^d	4.85 ^g	9.50 ^d	27.45 ^h	4.01 ^d	81.4	7.0
1% Gypsum	0.08 ^b	0.65 ^b	0.69 ^b	14.78 ^b	5.43 ^f	12.72 ^b	34.36 ^c	4.13 ^c	76.0	7.2
3% Pressmud	0.04 ^c	0.39 ^e	0.37 ^g	12.93 ^c	8.80 ^a	13.77 ^a	36.30 ^b	2.20 ⁱ	86.5	7.1
Control	0.10 ^a	3.77 ^a	2.05 ^a	21.58 ^a	7.91 ^b	13.97 ^a	49.38 ^a	11.99 ^a		6.0
C.D. (P=0.05)	0.00	0.01	0.02	0.58	0.23	0.92	0.06	0.01		0.1
SE(m) ±	0.00	0.00	0.01	0.19	0.08	0.31	0.02	0.00		0.0
SE(d)	0.00	0.01	0.01	0.27	0.11	0.44	0.03	0.01		0.1
C.V.	5.4	0.90	1.48	2.51	2.13	4.56	0.12	0.17		1.1

Table 3: Sequential extraction of Ni spiked soil at 60 days of incubation period treated with different ameliorants

Treatment	Water soluble	Exchange-able	Carbonate bound	Oxide bound	Organic bound	Residual	Total Ni (mg kg ⁻¹)	Mobile Pool of Ni (%)	Reduction (%) Mobile Ni	pH(1:1)
1% Lime	0.00	0.04 ^f	0.75 ^b	10.63 ^d	4.57 ^e	10.1 ^c	26.09 ^e	3.03 ^e	81.9	7.9
1% KH ₂ PO ₄	0.02 ^c	0.25 ^d	0.52 ^d	9.77 ^e	5.93 ^c	12.88 ^a	29.37 ^d	2.69 ^f	81.9	7.5
5% Biochar	0.01 ^d	0.28 ^c	0.55 ^{cd}	8.63 ^f	4.92 ^d	7.97 ^d	22.36 ⁱ	3.76 ^b	80.8	7.2
10% FYM	0.01 ^d	0.253 ^{cd}	0.37 ^e	9.63 ^e	4.7 ^{de}	9.93 ^c	24.89 ^f	2.53 ^g	85.6	7.4
2% Vermicompost	0.01 ^d	0.18 ^e	0.23 ^f	10.63 ^d	3.63 ^f	9.6 ^e	24.28 ^g	1.73 ^h	90.4	7.4
1% Zeolite	0.01 ^d	0.49 ^b	0.35 ^e	11.2 ^c	3.73 ^f	8.17 ^d	23.95 ^h	3.55 ^d	80.5	7.2
1% Gypsum	0.06 ^b	0.52 ^b	0.58 ^c	13.87 ^b	4.47 ^e	12.03 ^b	31.53 ^c	3.68 ^c	73.5	7.3
3% Pressmud	0.02 ^c	0.25 ^d	0.27 ^f	11.13 ^c	7.83 ^a	13.07 ^a	32.57 ^b	1.66 ⁱ	87.6	7.3
control	0.15 ^a	2.39 ^a	1.83 ^a	20.67 ^a	6.91 ^b	13.12 ^a	45.07 ^a	9.7 ^a		5.8
C.D. (P=0.05)	0.00	0.03	0.05	0.39	0.26	0.69	0.04	0.06		0.10
SE(m) ±	0.00	0.01	0.02	0.13	0.09	0.23	0.01	0.02		0.03
SE(d)	0.00	0.01	0.02	0.19	0.12	0.32	0.02	0.03		0.05
C.V.	1.04	3.07	4.56	1.93	2.90	3.69	0.08	0.99		0.80

Conclusions

Among the studied amendments pressmud, vermicompost, zeolites and lime showed a relatively higher efficacy in immobilizing Ni at different incubation intervals in spiked soils. Either of amendments which showed higher efficacy can be used to reduce the bio-available form of nickel. Thus,

these amendments have higher potential for an adequate use of immobilizing Ni in polluted soils in the near future.

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