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Identification of the solid phase in relation to the solubility of nickel in alluvial soils

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Abstract

The chemical equillibria between nickel (Ni) ion present in soil solution and solid phases govern the solubility *vis-a-vis* availability of Ni in soil. Therefore, stability of various Ni containing minerals in relation to pH was studied to identify the probable solid phases, which govern the solubility of Ni in some alluvial soils under intensive cultivation in and around Delhi. Free Ni^{2+} activity (pNi^{2+}) as estimated by Baker soil test, ranged from 13.1 to 16.2. Highest free Ni^{2+} activity (pNi^{2+} = 13.1) was recorded in industrial effluent irrigated soil collected from Sonepat, Haryana. Free Ni^{2+} activity was 13.6 in soil collected from agricultural lands of Keshopur, receiving irrigation through sewage effluents. Soils receiving irrigation through tube well water showed relatively lower free Ni^{2+} activity (pNi^{2+} = 14.6 to 16.2). Ni-ferrite in equilibrium with $Fe(OH)_3$ (amorphous) is likely to control the activity of Ni in two intensively Ni contaminated soil having pH around 8. Free Ni^{2+} activity is likely to be buffered by exchangeable Ni in soils having neutral pH.

Key words

Alluvial soil, Nickel, Solubility, Solid phase

Introduction

Nickel has long been considered an environmental pollutant. However, it was included in the list of essential plant nutrients in 1987 (Brown *et al*., 1987). It is an essential component of enzyme urease which is present in a wide range of plant species. Hence, it participates in nitrogen metabolism in plants (Singh *et al*., 2011). It has also been identified as the component of a number of enzymes, including glyoxalases, peptide deformylases, methyl reductases, ureases and few superoxide dismutases and hydrogenases (Kupper and Kroneak, 2007). High level of Ni is phytotoxic as well as zootoxic, especially to marine life. Excessive intake of Ni results in carcinogenesis and other metabolic complications in humans and animals (Das *et al*., 2008; Environment Agency, 2009).

Distribution of Ni in solid and solution phases in soil is generally governed by its chemistry in soil, which is ultimately reflected in its uptake by plant. There are several ways of understanding the chemical behaviour of Ni in soil which include simulation of thermodynamic stability of various Ni minerals and Ni ion activity in soil solutions; distribution of Ni in various discrete soil fractions; adsorption and desorption of Ni in soil, *etc.* Numerous minerals present in soil impose limits on the chemical composition of soil solution. It is well established that minerals precipitate, if soil solution is supersaturated, till attainment of equillibrium. Similarly, it dissolves if soil solution is under-saturated with respect of that mineral. The chemical equillibria between Ni ion present in soil solution and solid phases govern the solubility *vis-a-vis* availability of Ni in soil. The solubility of native forms of micronutrient cation in soil is determined by simultaneous equilibria of several competing reactions such as, surface chemical bonding, precipitation of solid phases, and solid phase chelation of metal cations. Free ion activity of an element in soil is a prerequisite for developing solubility relationship of that element in relation to probable minerals present in soils. There are number of methods (e.g. chealation method, Baker soil test method, Donnan membrane technique etc.) for determining the free metal ion concentration, but each method has its own advantage and disadvantage (Yi *et al*., 2007). Baker and Amecher (1981) developed an approach to soil testing, utilising the chelator DTPA which characterise both quantity and intensity parameters (free ion activity) of the elements in soil. No

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information is available on efficacy of this soil test to measure the activity of Ni^{2+} in soil. Hence, it was thought proper to evaluate efficacy of Baker soil test method in measuring free Ni^{+2} activity in relation to Ni uptake by plants, because it is well established that free ion activity of element in soil solution and plant uptake are closely correlated. In this paper thermodynamic stability models of various Ni containing minerals in relation to pH and Ni ion activity in soil solution were used to identify the specific mineral governing the solubility of Ni in these soils. The specific objectives of the present study were to evaluate the efficacy of Baker soil test in characterising available Ni in soil and to identify the solid phases which govern the solubility of Ni in soil. Alluvial soil was thought appropriate for such type of study, as this group of soil (e. g. Indo-Ganjetic plain) is reasonably fertile and contributes enormously towards India's food grain production.

Materials and Methods

Collection and analysis of soils : Fifteen bulk surface (0-15 cm) soil samples were collected from cultivated fields of different locations in and around Delhi. Out of these, four soil samples were collected from IARI farm which have been under intensive cultivation for more than seven decades. Five soil samples were collected from Keshopur, Delhi from agricultural lands receiving sewage irrigation for the last three decades. Four soil samples were collected from agricultural lands of Madanpur, Delhi which have been receiving irrigation either through tubewell water or river Yamuna. One soil sample collected from agricultural lands of Madanpur, Delhi which has been receiving sewage irrigation for last five decades. The remaining sample was collected from the agricultural fields adjoining ATLAS cycle factory, located at Sonipat, Haryana, which has been receiving industrial effluents for fifteen years. Soils were selected to ensure inclusion of variations in their physical and chemical properties covering normal and metal contaminated soil. The collected soil samples were air dried, ground and passed through a 2 mm sieve. These processed soil samples were used for greenhouse experiment as well as subsequent chemical analysis. Soil texture was determined by hydrometer method (Bouyoucos, 1962). Organic carbon content in soil was determined by wet oxidation method as outlined by Walkley and Black (1934). The cation exchange capacity (CEC) of the soil samples was determined by ammonium acetate method as described by Jackson (1973). Soils were extracted with citrate bicarbonate dithionite for free Fe_2O_3 and Al_2O_3 (Page, 1982). Iron content in the extract was estimated with the help of AAS and Al content was estimated colorimetrically using Aluminon method (Jayman and Sivasubramanium, 1974).

Determination of Ni ion activity in soil

Baker soil test equilibrium : Intensity factor of metal in experimental soils was evaluated following the procedure of Baker and Amacher (1981).

Baker soil test solution : 1.5734 g of DTPA was dissolved in 300 ml of distilled water with gentle heating. The solution was transferred quantitatively to a 1 litre volumetric flask; subsequently 10 ml of 0.25 *M* KCl, 10 ml of 1.0 *M* $MgCl_2$, 25 ml of 2.0 *M* $CaCl_2.2H_2O$ were added to DTPA solution in the volumetric flask. The contents were made up to 1 l.

Blank preparation : A blank soil test solution was prepared by pipeting 40 ml of distilled water, 5 ml of soil test solution and required amount of 0.0275 *M* triethanol amine into a polyethylene container to adjust pH of this solution at 7.30 $\pm$ 0.05. The final volume was maintained of 50.0 ml by adding distilled water.

Procedure : Five gram of processed soil (air-dried 2 mm sieved soil) was taken in a polyethylene container. Same amount of distilled water and 0.0275 *M* TEA was added, as determined in the blank preparation step. Then 5 ml of soil test solution was added. The contents were shaken for 1 hr and then allowed to stand for additional 23 hr. Small amount of the blank and sample solution were decanted for pH and EC determination. The remaining solution was filtered and used for analysis. Potassium (K) was determined by flame photometry, magnesium (Mg) and calcium (Ca) by atomic absorption spectroscopy (AAS) after necessary dilution and manganese (Mn), iron (Fe), zinc (Zn), copper (Cu), cadmium (Cd), lead (Pb), and nickle (Ni) by atomic absorption spectroscopy and aluminium (Al) by colorimetrically with aluminon (Page, 1982), respectively.

In Baker soil extract, at equilibrium, ions are distributed between soil and solution phases with no net movement of any ion from one phase to another. Some ions in solution remain chelated with DTPA (Baker solution) and others ions remain in free hydrated form. This distribution depends upon the amount of various ions in solution, strength of DTPA and stability constant for the formation of ion-DTPA complexes. The intensity factor of an ion is the relative partial free energy of an ion in the solution not chelated by DTPA. Based on this, a computer program in FORTRAN 77 was developed, where free metal ion activity could be estimated, based on equilibrium constant (thermodynamically characterized) through successive iterations (Datta *et al*., 2013). Free ion activity of metals was estimated by feeding the input data as obtained from Baker soil test extract to this computer programme (FORTRAN-77) (Table 1). The inputs of computer programme included pH, total concentration of Ca, Mn, Ni, Cu, Zn, Cd, Pb, Mg, Al, Fe and K in Baker extract and total concentration of Cl and DTPA in Baker solution. The free ion activity of these elements was expressed as negative logarithm of the metal ion activity ($M\ l^{-1}$). The concentrations of DTPA and Cl in Baker solution were 0.0004 M and 3710 mg l^{-1}, respectively.

Development of solubility diagram of Ni containing minerals: The solubility relationship of Ni containing minerals, *viz.* Ni-ferrite ($NiFe_2O_4$), Ni-aluminate ($NiAl_2O_4$) and Ni-silicate (Ni_2SiO_4) in relation to pH was developed (Sadiq and Enfield, 1984). The possibility of formation of these minerals not only depends on the

activity of Ni in soil, but is also affected by the activity of Fe, Al and Si.

Solubility relationships of Ni-ferrite, in equilibrium with amorphous Fe-oxide, can be developed as follows:

$NiFe_2O_4\,(C) + 8H^+ = Ni^{2+} + 2Fe^{3+} + 4H_2O$ (Log K° = 11.0) .....(1)

$2Fe(OH)_3\,(amorphous) + 6H^+ = 2Fe^{3+} + 6H_2O$ (Log K° = 7.08) ...(2)

(-) _____

$NiFe_2O_4\,(C) + 2H^+ = Ni^{2+} - 2\,H_2O$ (Log K° = 3.92).....(3)

or $Ni^{2+} / (H^+)^2 = 10^{3.92}$

or $Log\ Ni^{2+} = 3.92 - 2pH$..... (4)

From Equation (4), Log Ni^{2+} was computed at different pH of the soil and plotted in diagram (Fig. 1). Solubility of Ni-ferrite, Ni-aluminate and Ni-silicate, in equilibrium with relevant minerals was also developed, plotted and used for identification of most probable minerals which control the activity of Ni in soils under study (Fig. 1).

Greenhouse pot experiment : The greenhouse experiment was conducted in pots using all 15 experimental soils to assess the Ni uptake by plant using soybean (*Glycine max*) as a test crop. Soybean was selected as test crop because it is sensitive to Ni deficiency (Brown *et al*., 1987). Four kg of soil was poured into plastic pots. A uniform basal dose (150% of the recommended dose) of 20, 40 and 27 mg kg^{-1} of N, P_2O_5 and K_2O was added to the soil of each pot through urea, diammonium phosphate and muriate of potash, respectively. All the NPK fertilizers were added in solution form and thoroughly mixed with soil. Each treatment combination was replicated twice in a completely randomized design using 30 pots. The soil in each pot was then irrigated to field capacity with deionised water and incubated for one week at ambient temperature. Fifteen soybean seeds were sown and after two weeks of sowing, a uniform plant population (six plants pot^{-1}) was maintained in each pot. Pots were watered daily with the required amount of water on weight basis to maintain field capacity. The plants were harvested at the flowering stage, *i.e*., after 55 days of sowing.

Plant analysis : After harvesting, aerial parts of the plants were washed with deionised water and dried in hot air oven at 60-70 ˚C. After attaining constant weight, dry biomass yield was recorded. Dried plant samples were ground using mechanical grinder made up of stainless steel. Plant samples were then digested with di-acid mixture (HNO_3:$HClO_4$:: 10:4) and Ni content in the digest was determined by flame atomic absorption spectrophotometer (AAS).

Statistical analyses : Simple correlation coefficients (r) of nickel ion activity (pNi) with the Ni content in shoot of soybean was computed to evaluate the efficacy of Baker soil test in characterising available Ni in soil.

Results and Discussion

Physical and chemical properties of initial soil : Soil samples were selected for the present investigation so as to ensure wide variation in physical and chemical properties (Table 2). These

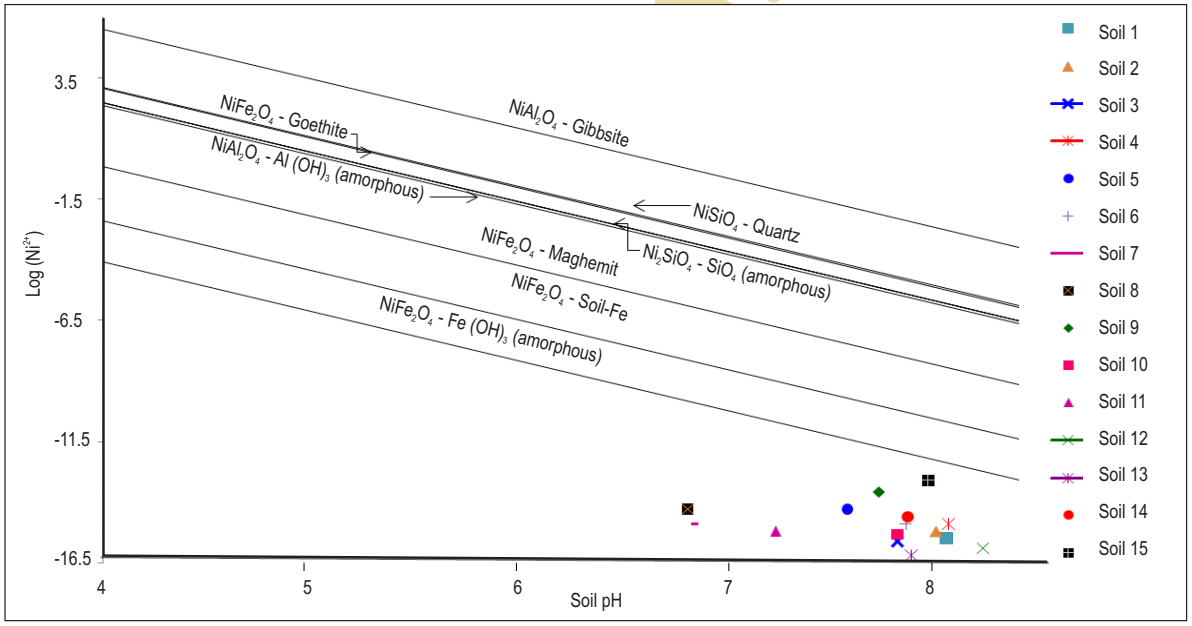

Fig. 1: Solubility digram of Ni containing minerals in equilibrium with Fe, Al, Si containing minerals

soils belonged to different textural classes. Soil pH was in neutral to alkaline range (pH 7.79 ± 0.11). All the soils were non-saline, as in evident from the values of EC (0.97± 0.26 dSm^{-1}). Soil organic carbon content was 0.53 ± 0.08 % and CEC of soils was 13.0 ±1.03 cmol (p+) kg^{-1}. There was a wide variation in both, clay as well as organic carbon content in soils, which was also reflected well in CEC. Free Fe_2O_3 and Al_2O_3 in soils were 0.30 ±0.10 and 0.12 ± 0.06%, respectively. DTPA extractable Ni in experimental soils showed considerable variation across the soils (1.39 ± 0.65 mg kg^{-1}).

Solubility relationships of nickel

Ni^{2+} activity in soils : Free Ni ion activity (intensity *i.e.* pNi^{2+}) values for different soils, as obtained with Baker soil test, are presented in table 3. Based on the intensity of Ni in soil solution, experimental soils can be arranged in decreasing order, soil 15> soil 9> soil 8 = soil 5> soil 14> soil 4 = soil 6 = soil 7> soil 11 = soil 2> soil 10> soil 1> soil 3> soil 12> soil 13. DTPA extractable Ni content followed more or less similar order, as obtained in the case of free Ni ion activity. Highest free Ni ion activity was observed in soil collected from Sonepat (soil 15). This is attributed to the fact that it had been receiving irrigation through industrial effluents emanating from the Atlas cycle factory. Free Ni^{2+} activity in soil 9 was 13.6. This soil was collected from the agricultural lands of Keshopur which has been receiving irrigation through sewage effluents for four decades. Hence, this soil showed relatively higher free Ni^{2+} activity as compared to other soils, except for soil 15. Rattan *et al*. (2005) reported that there was a substantial build-up of Ni in sewage irrigated soils of Keshopur. On the other hand, free Ni^{2+} activity in soils collected from agricultural lands which received irrigation through tube well water showed relatively lower values of free Ni^{2+} activity as compared to soils irrigated with sewage or industrial effluents. In case of soil 13 which was collected from Madanpur khadar, receiving irrigation through tube well water, showed lowest free Ni^{2+} activity among the experimental soils. Elevated level of free Ni^{2+} activity in agricultural soils receiving irrigation through waste water have also been reported by Yi *et al*. (2007).

Table 1 : Input data on metal concentrations (mg l^{-1}) and pH in Baker soil extract used for computing free Ni^{+} activity

Location	Ca	Mn	Ni	Cu	Zn	Cd	Pb	Mg	Al	Fe	K	pH
IARI farm,	55.5	5.06	0.04	0.07	0.24	0.01	0.14	15.0	0.02	0.93	11.2	7.42
New Delhi (4)	±11.5	±1.49	±0.004	±0.03	±0.04	±0.002	±0.05	±1.72	±0.004	±0.09	±4.70	±0.03
Keshopur,	74.4	2.75	0.14	0.55	1.61	0.007	0.12	19.8	0.4	6.38	14.4	7.36
Delhi (5)	±13.1	±0.95	±0.03	±0.19	±0.58	±0.001	±0.05	±3.14	±0.006	±0.75	±2.70	±0.06
Madanpur,	90.0	2.10	0.02	0.54	0.25	0.002	0.04	9.64	0.09	2.86	4.81	7.43
Delhi (5)	±18.0	±0.74	±0.007	±0.04	±0.05	±0.001	±0.01	±2.00	±0.06	±0.92	±3.15	±0.04
Sonepat,	48.8	1.28	1.90	1.16	6.05	0.23	0.02	15.4	0.04	1.16	12.2	7.45
Haryana (1)	±2.07	±0.03	±0.10	±0.16	±0.38	±0.001	±0.001	±1.45	±0.005	±0.16	±0.15	±0.005
Overall (15)	72.7	3.05	0.18	0.79	1.07	0.008	0.09	14.7	0.05	3.39	10.2	7.40
	±8.43	±0.61	±0.12	±0.56	±0.41	±0.001	±0.02	±1.65	±0.02	±0.70	±2.01	±0.02

Figures in parentheses indicate number of soil samples collected from respective locations

Table 2 : Physical and chemical properties of experimental soils

Location[$]	Mechanical composition			Textural class[#]	pH	EC	CEC	Organic	Free	Free	DTPA
	Clay (%)	Silt (%)	Sand (%)			($dS\ m^{-1}$)	(cmol (p+)kg^{-1})	carbon (%)	Fe_2O_3 (%)	Al_2O_3 (%)	extractable Ni (mg kg^{-1})
IARI farm,	26.5	15.0	58.5	Sandy loam (1),	8.07	0.37	13.7	0.46	0.32	0.06	0.31
New Delhi (4)	±4.16	±2.65	±4.30	Sandy clay loam (3)	±0.06	±0.13	±2.27	±0.07	±0.04	±0.004	±0.04
Keshopur,	15.0	24.3	60.6	Silt loam (1), 7.43	1.74	15.8	0.74	0.17	0.04	1.79	
Delhi (5)	±1.81	±11.6	±12.3	Sandy loam (4)	±0.23	±0.66	±1.38	±0.07	±0.01	±0.005	±0.30
Madanpur,	7.62	33.0	59.3	Silt loam (2), Sandy	7.89	0.76	10.3	0.37	0.14	0.24	0.15
Delhi (5)	±2.45	±13.2	±12.4	loam (2), Sand (1)	±0.16	±0.18	±1.72	±0.20	±0.03	±0.18	±0.04
Sonepat,	18.8	30.5	50.6	Loam (1)	8.03	0.50	12.2	0.62	1.64	0.13	9.91
Haryana (1)	±0.05	±0.50	±0.55		±0.03	±0.005	±0.20	±0.02	±0.04	±0.005	±0.005
Overall (15)	15.9	25.1	58.9	Sandy loam (7), Silt	7.79	0.97	13.0	0.53	0.30	0.12	1.39
	±2.39	±5.76	±5.51	loam (3), Sandy clay loam (3) Loam (1), Sand (1)	±0.11	±0.26	±1.03	±0.08	±0.10	±0.06	±0.65

[$]Figures in parentheses indicate number of soil samples collected from respective locations; [#]figures in parentheses indicate number of soil samples belong to respective textural classes

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Table 3 : Nickel ion activity in experimental soils and Ni content in shoot of soybean grown thereon

Soil No.	Ni content in shoot (mg kg^{-1})	Ni ion activity (pNi)*
1	0.61	15.5
2	0.18	15.2
3	0.47	15.6
4	0.39	14.9
5	1.28	14.3
6	0.28	14.9
7	0.80	14.9
8	6.31	14.3
9	0.67	13.6
10	0.21	15.3
11	1.43	15.2
12	0.16	15.9
13	0.19	16.2
14	0.17	14.6
15	6.24	13.1

* Nickel ion activity (pNi) was estimated by Baker soil test

Efficacy of Baker soil test : An attempt was made to evaluate the efficacy of Baker soil test for characterising the free ion activity vis-a-vis phytoavailability of Ni in soil, through simple correlation analysis. Results indicated that free Ni^{2+} activity (pNi^{2+}) was positively correlated with plant Ni content (r = 0.65; significant at 1% probability level). For interpretation of soil fertility status (availability of nutrients), both quantity and intensity parameters of Baker soil test are required to be taken into consideration (Lee and Doolittle, 2006). This emphasized that lowest levels did not always imply that the soil was deficient for crop production nor did high test values necessarily mean toxicity to crops. Deficiency symptoms and yield decrease could be anticipated when quantity and intensity factor levels were low on sandy soils with low CEC and organic matter levels, heavily limed or alkaline soils and highly weathered acid soil. In the present investigation, as high as 42% variation in Ni content in soybean plant could be accounted for intensity factor of Ni alone, even the quantity factor has not been taken into account. This shows that Baker soil test was reasonably effective in determining free ion activity of Ni *i.e.* intensity factor. Free metal ion activity has been shown to be the key factor in determining metal bioavailability and toxicity in most of the earlier studies (Cances *et al*., 2003).

Solid phases : Aluminium and iron are the two major soil elements that react with heavy metals. Silica is the second most abundant element in the crust. Hence, in order to identify Ni containing mineral responsible for controlling free Ni^{2+} activity in soil solution, solubility relationship of Ni-aluminate ($NiAl_2O_4$), Ni-ferrite ($NiFe_2O_4$) and Ni-silicate (Ni_2SiO_4) with respect to soil pH were developed (Fig. 1). Solubility line of Ni-ferrite was developed in equllibrium with $Fe(OH)_3$ (amorphous), $Fe(OH)_3$ (soil-Fe), 1/2γ-Fe_2O_3 (magnetite), 1/2 α- Fe_2O_3 (hematite), α- FeOOH (goethite), γ- FeOOH (lepidocrosite). Activities of Ni in experimental soils as estimated by Baker soil test, were super imposed in Fig. 1. By examining the proximity of these points to solubility lines, the solid phases supposed to control the solubility of Ni in respective soils, were identified. The results indicate that activity of Ni in all the soils lying below the solubility line of $NiFe_2O_4$-$Fe(OH)_3$ (amorphous) line. As the solubility of Fe-oxide increased the solubility of Ni-ferrite in equilibrium with Fe-oxides decreases. Generally soil-Fe governs the solubility of Fe in soils. However, in the present study soil 9 and 15 maintained free Ni^{2+} activity close to the solubility line of $NiFe_2O_4$-$Fe(OH)_3$ (amorphous), indicating that this Ni containing mineral, in equilibrium with $Fe(OH)_3$ (amorphous) maintained the activity of Ni in soil. $Fe(OH)_3$ (amorphous) may be expected to govern the solubility of Fe in soils receiving particularly sewage sludge and industrial effluents as compared to the soils that have been receiving irrigation through tubewell water. However, Ni ion activities in other sewage irrigated soils, having pH around 8, also appeared to be limited by $NiFe_2O_4$-$Fe(OH)_3$ (amorphous) line. In tubewell irrigated soils, having pH 8, it is unlikely that activity of Fe in soil is governed by $Fe(OH)_3$ (amorphous) owing to the fact that the activity of Fe is lower than that of sewage irrigated soil. In such soils, it was difficult to identify solid phases which govern the solubility of Ni in soils. Three soils *viz*. soil 7, 8 and 11 had pH ≤ 7.3. There the activity of Ni was much below the solubility line of $NiFe_2O_4$-$Fe(OH)_3$ (amorphous). Free Ni^{2+} activity in these soils may be buffered by exchangeable Ni in soils. Activity of Fe in none of these soils, with reference to the respective pH, except soils 7, 8 and 11 approached the level of activity of Fe which would be maintained by goethite or maghemite. Hence, it obvious that there was no possibility of formation of either Ni-silicate or Ni-aluminate in these soils. Thus, it appears that Ni-silicate or aluminate can't form in soils under study. Oxides and hydroxides of Ni^{3+} are very soluble even under highly oxidised condition; there is remote possibility of formation of these minerals in soils under study. On the other hand, formation of oxides and hydroxides of Ni^{2+} requires very high concentration of Ni, about 1 mole, which is far from reality for these soils. Hence, it is unlikely to form these minerals in soil as well. Solubility of $NiCO_3$ is far more than Ni-ferrite in equilibrium with amorphous or soil–$Fe(OH)_3$. Similarly Ni-phosphate in equilibrium with either strengite, variscite or Ca-phosphate are less stable than Ni-ferrite in equilibrium with amorphous or soil –$Fe(OH)_3$. Hence, these minerals cannot be responsible for controlling solubility of Ni^{2+} in these soils. Moreover Ni-phosphate may form in acids soils only. For formation of sulphates of Ni requires unusually high activity of Ni. Therefore, precipitation of this mineral is of distant possibility. Under much reduced condition Ni-sulphide can be formed. In such a condition other metals like Zn, Cu, Fe, Mn, Pb, Cd may also compete with Ni for the formation of sulphide mineral. Soils were collected for this study from well drained agricultural lands and most of these soils are medium to light in texture. Hence, again there is a remote possibility of an extremely reduced prevailing condition which favours the formation of Ni sulphide.

Some study indicated that formation of mixed metal layered double hydroxide decreased Ni solubility in soil (Peltier *et al*., 2006). Hydrous ferrous oxide was also identified as one of the most important sorbents in smelter contaminated soils (Yi *et al*., 2007). Besides, Ni has been commonly found predominantly in the residual and Fe-Mn oxide fraction (Kabata-Pendias and Mukherjee, 2007).

It can be concluded that in all probabilities, activity of Ni particularly in intensively contaminated soil having pH around 8, is limited by solubility of Ni-ferrite in equilibrium with $Fe(OH)_3$ (amorphous). In case of other soils, exchangeable Ni may control Ni^{2+} activity in soil solution. Such information may be useful in managing both, deficiency and toxicity of Ni in agricultural soils.

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References

Baker, D.E. and M.C. Amacher: The development and interpretation of a diagnostic soil-testing program. Pennsylvania State University Agricultural Experiment Station Bulletin 826. State College, PA (1981).

Baker, D. E.: Baker Soil Test Theory and applications, 1990.*Commun. Soi.Sci. Pl. Anal.,* **21**:981-1008 (1990).

Boycous, G. J.: Hydrometer method improved for making particle size analysis of soils. *Agro. J.,* **54,** 464 (1962).

Brown, P. H., R.M. Welch and E.E. Carry: Nickel: A micronutrient essential for higher plants. *Pl. Physiol.,* **85**, 801-803 (1987).

Cancès, B., M. Ponthieu, M. Castrec-Pouelle, E. Aubry, and M.F. Benedetti: Metal ions speciation in a soil and its solution: Experimental data and model results. *Geoderma,* **113**, 341–355(2003).

Das, K.K., S.N. Das and S.A. Dhundasi: Nickel, its adverse health effects and oxidative stress. *Ind. J. Med. Res.,***128**, 412-425 (2008).

Datta, S.P., B.L. Meena and R.K. Rattan: Development of a computer program for calculating metal ion activity using Baker soil test. *J. Ind. Soc.Soil. Sci.,* **61**, 47-50 (2013).

Environment Agency: Contaminants in soil: updated collation of toxicological data and intake valuesfor humans. Nickel. *Sci. Report,* (2009). SC050021/SR TOX8. Bristol: Environment Agency.

Jackson, M.L.: Soil Chemical Analysis. Prentice Hall of India Private Limited, New Delhi (1973).

Jayman T.C.Z. and S. Sivasubramaniam: The use of ascorbic acid to eliminate interference from iron in the aluminon method for determining aluminium in plant soil extracts. *Analyst,* **99**, 296-301(1974).

Kabata-Pendias, A. and A.B. Mukherjee: Trace elements from soil to Human. Berlin: Springer-Verlag (2007).

Kupper, H. and P.M.H. Kroneck: In: Metal ions in Life Sciences (Eds: A. Sigel, H. Sigel and R.K.O. Sigel). Vol. 2, John Wiley and Sons, Chichester, UK, pp. 31-62 (2007).

Lee, J.H. and J.J. Doolittle: Investigation of cadmium and zinc interactions in soils using desorption isotherms. *Korean J. Environ. Agric.*, **25**, 157-163 (2006).

Page, A.L.: Methods of Soil Analysis: Chemical and Microbiological Properties. Vol. 9, Soil Science Society of America, Madison, WI (1982).

Peltier, E., R. Allada, A. Navrotsky and D. Sparks: Nickel solubility and precipitation in soils: A thermodynamic study. *Clays Clay Minerals,* **54**, 153-164 (2006).

Rattan, R.K., S.P. Datta, P.K. Chhonkar, K. Suribabuand and A.K. Singh: Long–term impact of irrigation with sewage effluents on heavy metal content in soils, crops and groundwater– a case study. *Agri. Ecosys. Env.,***109**, 310–322 (2005).

Sadiq, M. and C.G. Enfield: Solid phase formation and solution chemistry of nickel in soils: 1. Theoretical. *Soil. Sci.,***138**, 262–270 (1984).

Singh, R.P., S.K.S. Chandel, P.K. Yadav and S.N. Singh: Effect of Ni on nitrogen uptake and yield of wheat (*Triticum aestivum*). *Indian. J. Sci. Res.*, **2**, 61-63 (2011).

Walkley, A. and I.A. Black: An examination of the Degtjareff method for determining soil organic matter and a proposed modification of the chromic acid titration method. *Soil. Sci.,* **37**, 29-38(1934).

Yi,L., Y.Hong, D. Wang and Y. Zhu: Determination of free heavy metal ion concentrations in soils around a cadmium rich zinc deposit. *Geochemical J.,* **41**, 235-240 (2007).

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