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EFFECT OF NICKEL AND FYM ON SPINACH AND DIFFERENT FORMS OF NICKEL IN *FLUVENTIC USTOCHREPTS* OF MIDDLE GUJARAT

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ABSTRACT

The effect of Ni (0, 5, 10, 20, 40 and 80 mg kg^{-1} soil) in presence and absence of FYM (0 and 1 per cent) on different forms of Ni was studied in industrial effluent irrigated (contaminated) and tube well water irrigated (non-contaminated) soils after spinach during 2003 at Anand Agricultural University, Anand. Application of Ni significantly increased different forms of Ni viz., exchangeable, carbonate, oxide, organically bound, residual and total in both the soils. The application of FYM significantly increased exchangeable, oxide and organically bound Ni under contaminated soil, whereas it was true for all the fractions, except residual and total Ni in case of non-contaminated soil. Application of higher rate of Ni (80 mg kg^{-1}) increased exchangeable, carbonate, oxides, organically bound, residual and total Ni by about 1.5, 3.0, 26.3, 7.0, 0.3 and 1.7 times, respectively over Ni_0. Similarly, the corresponding values for non-contaminated soil were 0.4, 2.0, 8.3, 3.5, 2.1 and 2.7. Further, except residual fraction of Ni, all other fractions showed more enrichment in contaminated soil than normal soil. Interaction effect of Ni and FYM was significant in altering carbonate, oxide and organic Ni in contaminated soil, while exchangeable, carbonate, oxides and organically bound Ni were affected significantly in case of non-contaminated soil. With the applications of Ni, the overall distribution of the different fractions suggested that the externally added Ni enriched the fractions viz., carbonate and oxide forms with reduction in residual form towards the initial

value. However, exchangeable form did not show much change as noticed in the situation wherein Ni was not added. Organically bound Ni was enriched both in absence and presence of Ni with FYM and the corresponding improvement was to the tune of 10.2 and 31.2 per cent over no FYM

INTRODUCTION

Estimation of total metal concentration in soil can only provide information on the contamination load and identification of areas of significant contamination. But it does not provide any information regarding the mobility, plant availability, chemical reactivity and biological effects of metal. It is necessary to understand and differentiate the different physico-chemical forms of metals in soils and sediments, to assess the agricultural and environmental impacts of trace metals. Trace metals like Ni present in soils are found in a variety of physico-chemical forms (Berti and Jacobs, 1996).

Availability of Ni in soil is a part of its presence among different forms. Fractionation of Ni from soil is a useful tool for determining different forms of Ni in soil. Presence of phosphate, carbonate and complexants (EDTA, citric acid and oxalic acid) govern the availability of Ni in a soil. To elucidate the fractionation of the heavy metals between different forms in soils, several sequential extraction or fractionation schemes have been proposed (Tessier *et al.* 1979). The most frequently used extraction schemes divide the heavy metals in the soil into several fractions. These fractions are characterized by the extractant used to dissolve the metals, and the four most common fractions are exchangeable, oxidizable, reducible and residual.

Therefore, the aim of this work was to quantify the contribution of different Ni fractions of total Ni due to different levels of Ni in presence of FYM on effluent irrigated contaminated and well water irrigated normal (non-contaminated) *Fluventic Ustochrepts* soils after spinach.

MATERIALS AND METHODS

The bulk soil samples were collected from industrial effluent irrigated fields (contaminated soil) close to effluent channel, where farmers are using waste water for irrigation for more than 30 years. Simultaneously, bulk soil samples from tube well water irrigated fields (non-contaminated soil) of the same area were also collected as a reference sample for pot study.

The important initial soil physical properties like mechanical separates (sand, silt and clay) and chemical properties i.e. pH, EC (1:2.5 soil: water ratio), organic carbon (OC), available nutrients *viz.*, P_2O_5, K_2O, S, DTPA (Diethyleme Triamine Penta Acetic acid) extractable micronutrients and heavy metals (Lindsay and Norwell, 1978) and nickel fractionations (Tessier *et al.* 1979) were determined as per the standard methods and the values are presented in Table 1.

The soils collected were sandy loam in texture, having slightly alkaline reaction but no salt accumulation in normal soil while in case of industrial effluent irrigated soil, the reaction was near neutral with salt accumulation. The available micronutrients and heavy metals were higher in contaminated soil as compared to non-contaminated soil (Table 1).

Table 1

Physico-chemical characteristics of initial soil

Sr. No.	Parameter and method	Value	
		Contaminated	Non- contaminated
1.	Texture and classification	Sandy loam	
2.	$pH_{2.5}$	6.84	8.14
3.	$EC_{2.5}$ (dSm^{-1})	0.93	0.19
4.	Organic carbon (g kg^{-1})	7.80	4.30
5.	Av. P_2O_5 (kg ha^{-1})	89.6	75.9
6.	Av. K_2O (kg ha^{-1})	1198	791
7.	Av. S (0.15% $CaCl_2$) (mg kg^{-1})	57.9	8.4
8.	DTPA - Ni (mg kg^{-1})	0.86	0.43
9.	Fractions of Ni (mg kg^{-1})		
	Exchangeable	5.68	5.36
	Carbonate bound	4.72	4.68
	Fe – Mn oxides	7.40	5.30
	Organically bound	3.80	2.95
	Residual	23.70	10.46
	Total	45.30	28.75

The experiment was conducted in a pot house of the Micronutrient Project (ICAR), Anand Agricultural University, Anand during 2003-04. The spinach was grown for 60 days with 6 levels of Ni (0, 5, 10, 20, 40 and 80 mg kg^{-1}) through $NiCl_2 \cdot 6H_2O$ in presence (1%) and absence of FYM. These twelve treatment combinations were studied on two soils in the experiment with Factorial Completely Randomized Design (FCRD2).

The nickel was applied in the solution form of $NiCl_2.6H_2O$ and required quantities of the chemicals were well mixed with the soil as per the treatments. In case of FYM, considering the moisture content, its required quantity was applied to the respective pots as per treatment. The pots were watered to attain field capacity. The recommended quantities of N - P- K fertilizers were applied. The pots were irrigated with water as and when required to maintain the sufficient moisture content in the soil during growing period of the crop. Besides agronomic practices, plant protection measures were also taken as and when required.

After harvesting of spinach, soil samples were collected by the tube auger by making four random spots in each pot and processed by air drying and ground to pass through 2 mm stainless steel sieve. The chemical analysis of the samples was carried out as per the standard methods. Total heavy metals and Ni fractions were determined following the methods given by Tessier *et al.* (1979).

RESULTS AND DISCUSSION

The characteristics of contaminated and non-contaminated soils are given in

Table 2

Effect of Ni on different Ni fractions after spinach

Ni (mg kg⁻¹ soil)	Contaminated soil			Non-contaminated soil		
	FYM (g 100g⁻¹ soil)					
	F_0	F_1	Mean	F_0	F_1	Mean
Exchangeable Ni (µg g⁻¹)						
Ni_0	5.61	5.21	5.41	4.48	5.19	4.83
Ni_5	6.47	5.92	6.19	5.03	5.56	5.29
Ni_{10}	6.76	6.29	6.53	5.56	5.36	5.46
Ni_{20}	7.87	7.65	7.76	5.72	5.76	5.74
Ni_{40}	10.49	10.35	10.42	6.11	5.65	5.88
Ni_{80}	13.89	13.23	13.56	6.80	7.15	6.97
Mean	8.52	8.11	8.31	5.62	5.78	5.70
	F	Ni	F x Ni	F	Ni	F x Ni
S. Em.(±)	0.24	0.41	0.58	0.07	0.12	0.17
CD @ 5%	NS	1.19	NS	NS	0.35	0.49
CV %	12.1	5.1				
Carbonate Ni (µg g⁻¹)						
Ni_0	3.81	3.96	3.89	3.97	3.97	3.97
Ni_5	5.15	4.27	4.71	4.14	5.73	4.94
Ni_{10}	5.32	5.17	5.25	6.84	6.44	6.64
Ni_{20}	6.71	9.31	8.01	8.53	8.41	8.47
Ni_{40}	12.15	15.40	13.77	10.07	8.49	9.28
Ni_{80}	14.88	15.87	15.37	11.67	13.52	12.9
Mean	8.00	9.00	8.50	7.54	7.76	7.65
	F	Ni	F x Ni	F	Ni	F x Ni
S. Em.(±)	0.48	0.82	1.17	0.09	0.15	0.22
CD @ 5%	0.65	1.12	1.58	NS	0.45	0.64
CV %	8.2	5.3				
Oxides Ni (µg g⁻¹)						
Ni_0	1.57	1.13	1.35	3.30	3.60	3.45
Ni_5	4.13	3.17	3.65	5.37	4.97	5.17
Ni_{10}	6.27	5.87	6.07	8.17	6.37	7.27
Ni_{20}	11.07	8.80	9.93	11.83	11.27	11.55
Ni_{40}	19.43	13.93	16.68	19.50	17.57	18.53
Ni_{80}	40.17	33.63	36.90	35.17	29.33	32.25
Mean	13.77	11.09	12.43	13.89	12.18	13.04
	F	Ni	F x Ni	F	Ni	F x Ni
S. Em.(±)	0.39	0.68	0.96	0.37	0.64	0.90
CD @ 5%	1.14	1.98	2.80	1.07	1.86	2.63
CV %	13.3	12.0				

Table 1. The change in different Ni fractions determined after spinach in both effluent irrigated contaminated and well water irrigated non-contaminated soils are given in Tables 2 & 3.

Effect of Nickel

The effect of different levels of Ni was significant on different fractions of Ni in both the soils after spinach. Among the different fractions, Fe-Mn oxides bound

Table 3
Effect of Ni on different Ni fractions after spinach

Ni (mg kg^{-1} soil)	Contaminated soil			Non-contaminated soil		
	FYM (g 100g^{-1} soil)					
	F_0	F_1	Mean	F_0	F_1	Mean
Organic Ni (μg g^{-1})						
Ni_0	0.91	1.04	0.98	1.68	1.77	1.73
Ni_5	1.07	1.28	1.18	2.10	1.87	1.98
Ni_{10}	1.29	1.93	1.61	2.25	2.47	2.36
Ni_{20}	1.98	2.58	2.28	4.13	3.90	4.02
Ni_{40}	3.03	3.90	3.47	4.22	4.90	4.56
Ni_{80}	6.13	8.28	7.21	7.7	9.33	8.55
Mean	2.40	3.17	2.79	3.69	4.04	3.87
	F	Ni	F x Ni	F	Ni	F x Ni
S. Em.(±)	0.07	0.13	0.19	0.06	0.10	0.14
CD @ 5%	0.22	0.38	0.54	0.17	0.30	0.42
CV %	11.4	6.5				
Residual Ni (μg g^{-1})						
Ni_0	32.26	33.66	32.96	14.06	13.81	13.94
Ni_5	31.52	34.53	33.03	15.04	14.37	14.70
Ni_{10}	31.87	34.07	32.97	13.85	17.70	15.78
Ni_{20}	35.71	35.82	35.77	16.45	18.16	70.30
Ni_{40}	37.39	39.75	38.57	25.11	30.05	27.58
Ni_{80}	42.43	48.16	45.29	41.10	44.00	42.55
Mean	35.20	37.66	36.43	20.34	23.02	21.97
	F	Ni	F x Ni	F	Ni	F x Ni
S. Em.(±)	1.18	2.04	2.89	1.12	1.94	2.74
CD @ 5%	NS	5.96	NS	NS	5.65	NS
CV %	13.7	21.6				
Total Ni (μg g^{-1})						
Ni_0	44.17	45.00	44.58	27.50	28.33	27.92
Ni_5	48.33	49.17	48.75	31.67	32.50	32.08
Ni_{10}	52.50	53.33	52.92	36.67	38.33	37.50
Ni_{20}	63.33	64.17	63.75	46.67	47.50	47.08
Ni_{40}	82.50	83.33	82.92	65.00	66.67	65.83
Ni_{80}	117.5	119.17	118.33	102.5	103.33	102.92
Mean	68.06	69.03	68.54	51.67	52.78	52.22
	F	Ni	F x Ni	F	Ni	F x Ni
S. Em.(±)	1.16	2.01	2.85	0.92	1.60	2.26
CD @ 5%	NS	5.87	NS	NS	4.66	NS
CV %		7.2				

Ni was the highest followed by carbonate, exchangeable and organically bound Ni in both the soils after spinach (Fig. 1). Application of 80 mg kg^{-1} Ni increased exchangeable, carbonate, oxides, organically bound, residual and total Ni by about 1.5, 3.0, 26.3, 7.0, 0.3 and 1.7 times, respectively over Ni_0. Similarly, the corresponding values for non-contaminated soil were 0.4, 2.0, 8.3, 3.5, 2.1 and 2.7 (Table 3 and 4). Thus, it was noticed that oxides bound Ni enrichment was quite higher in contaminated soil than non-contaminated. Further, except re-

Table 4

Correlation coefficient (r) of DTPA-Ni with different Ni fractions

Parameters	Exchangeable	Carbonate	Oxide	Organic	Residual	Total
Contaminated	0.986**	0.929**	0.981**	0.954**	0.924**	0.993**
Non-contaminated	0.917**	0.942**	0.934**	0.984**	0.973**	0.975**

Table 5

Effect of Ni and FYM on leaf yield of spinach

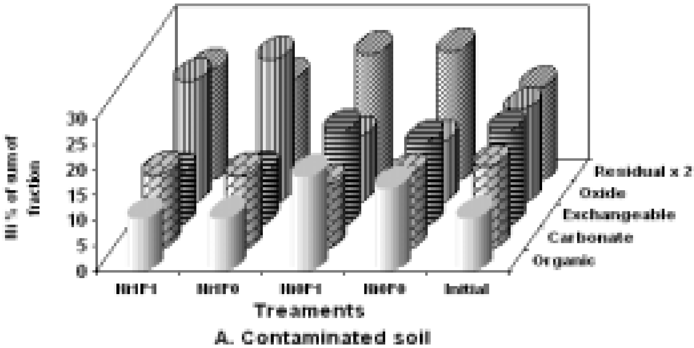
Ni ($mg\ kg^{-1}$ soil)	Contaminated soil			Non-contaminated soil		
	FYM ($g\ 100g^{-1}$ soil)					
	F_0	F_1	Mean	F_0	F_1	Mean
	Green leaf yield ($g\ pot^{-1}$)					
Ni_0	67.51	68.65	68.08	82.41	85.64	84.03
Ni_5	69.80	71.04	70.42	83.19	86.01	84.60
Ni_{10}	70.61	71.74	71.18	86.09	93.80	89.95
Ni_{20}	65.11	70.91	68.01	83.06	90.36	86.71
Ni_{40}	61.66	68.95	65.13	77.83	85.95	81.89
Ni_{80}	53.14	63.58	58.36	68.94	77.50	73.22
Mean	64.64	69.14		80.25	86.54	
	F	Ni	F x Ni	F	Ni	F x Ni
S. Em.(±)	0.67	1.16	1.63	1.81	3.14	4.44
CD @ 5%	1.95	3.37	4.77	5.29	9.17	NS
CV %		4.2			10.2	

sidual fraction of Ni, all other fractions showed more enrichment under contaminated soil condition than non-contaminated soil.

Effect of FYM

The data presented in Tables 3 and 4 indicate that the effect of FYM application was significant on Ni fractions viz., carbonate, oxides and organically bound Ni in contaminated soil, while incase of normal soil, the significant effect of FYM was noticed for oxides and organic forms only. The application of FYM @ 1% had improved Ni availability significantly for exchangeable, oxide and organically bound Ni under contaminated soil; whereas it was true for all fractions, except residual and total Ni in case of non-contaminated soil.

The results revealed that organic fraction of Ni accounted only for 4 per cent of the total Ni. The higher proportion of metals in inorganic or amorphous sesquioxides forms has also been reported by Pal *et al.* (1997). Organically bound Ni in presence of FYM was recorded higher by 31.3 and 7.5 per cent than no FYM for contaminated and non-contaminated soil, respectively after spinach (Fig.3). The high percentage in organically bound Ni in contaminated soil could be attributed to relatively more Ni ions available to be complexed with organic colloids. This could be due to comparatively higher saturation of available sites for fixation as a result of initial contamination.



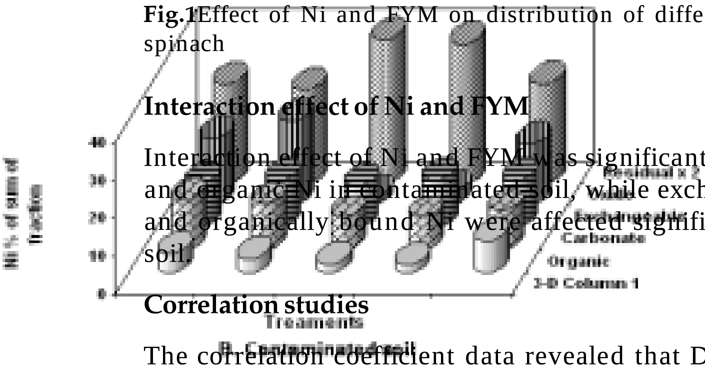


Fig.1 Effect of Ni and FYM on distribution of different Ni forms after harvest of spinach

Interaction effect of Ni and FYM

Interaction effect of Ni and FYM was significant in altering carbonate, oxide and organic Ni in contaminated soil, while exchangeable, carbonate, oxides and organically bound Ni were affected significantly in non-contaminated soil.

Correlation studies

The correlation coefficient data revealed that DTPA-Ni showed significant positive relationship with all forms of Ni viz., exchangeable, carbonate, oxides, organic and total Ni (Table 4). Thus, it clearly revealed that the different forms of Ni were in equilibrium with that available fraction i.e. DTPA – Ni which might contribute towards enrichment of this fraction upon its depletion due to plant uptake.

Per cent distribution of Ni fractions

The data on different forms of Ni in contaminated and non-contaminated soils as influenced by Ni and FYM application after spinach were computed for its per cent distribution and depicted in Fig 1. The results revealed that Ni was mainly associated with Fe and Mn oxides followed by carbonate, exchange-able and organic fractions. Narwal *et al.* (1993) also reported that the percent-

Fig. 2 Relative per cent of different fractions of Ni in contaminated (S1) and non-contaminated (S2) soils

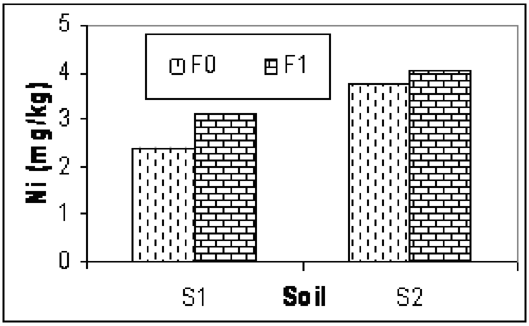


Fig. 3 Effect of FYM on organic Ni in contaminated (S1) and non-contaminated (S2) soils

age of total Ni extracted by $NH_4OH.HCl$ (in HOAc) was greater than all other fractions.

It was observed that due to growing of spinach, there was a decrease in the fractions like carbonate, oxide and organic bound Ni with the corresponding increase in residual fraction when Ni was not added and the exchangeable form showed very little change (Fig. 1). With the applications of FYM, organically bound Ni was enriched both in absence and presence of Ni and the corresponding improvement was to the tune of 10.2 and 31.2 per cent over no FYM.

In case of Ni application, the overall distribution of the different fractions suggested that the externally added Ni enriched the fractions viz., carbonate and oxide forms with reduction in residual form towards the initial value. However, exchangeable form did not show much change as noticed in the situation wherein Ni was not added. The per cent distribution of carbonate and oxide bound Ni forms under Ni_1F_0 revealed their enrichment with Ni, while FYM (Ni_1F_1) addition enhanced Ni concentration more in organically bound form and caused depression in per cent distribution of oxide bound Ni leading towards initial pattern of distribution. Further, in all the situations, exchangeable Ni was little affected. Thus, the study revealed that the changes in Ni fractions due to Ni and FYM addition to contaminated soil were mostly confined to the forms other than exchangeable after spinach.

In case of non-contaminated soil, the changes in per cent distribution of different Ni forms after spinach were not similar to that of contaminated soil condition (Fig. 1). The major difference was noticed in exchangeable form, which was affected to a greater extent due to Ni addition with and without FYM. The initial distribution of different fractions viz., exchangeable, carbonate, oxides, organic and residual Ni was 18.6, 16.3, 18.3, 10.3 and 36.4 per cent of total Ni (28.75 mg kg^{-1}), respectively. After spinach, the changes were towards decrease in per cent distribution of carbonate, oxide and organic bound Ni fractions without Ni in non-contaminated soil which were comparatively lower than contaminated soil. In case of Ni addition, a reverse trend in carbonate and oxide forms was noticed. Similarly in contaminated soil, enrichment in organic Ni was found due to FYM both in absence and presence of Ni. The improvement in organically bound Ni was to the tune of 7.5 and 3.2 per cent with and without Ni, respectively. Therefore, the results indicated that the accumulation of Ni through the use of contaminated effluents over years might cause toxic effect of Ni in crops due to possible enrichment of forms like carbonates and oxides bound Ni in contaminated soil.

The fixation in terms of enrichment of externally added metal was more possible with different forms like carbonate and oxides in non-contaminated soil due to more available free sites with these oxides compared to contaminated soil. There might be a possibility of initial enrichment of contaminated soil due to addition of metals during the process of contamination through effluent irrigation. The situation might have left less of the available sites free for fixation upon addition of Ni and therefore free Ni ions might have exhibited adverse and toxic effect on spinach growth and yield (Table 5) even at lower level of Ni addition than that observed under non-contaminated soil. The fractions viz., exchangeable, carbonate, oxides and organically bound showed more enrichment due to Ni application in contaminated soil than non- contaminated soil. The organically bound Ni was more enriched due to application of FYM. Thus, the role of FYM was obvious under both the soil conditions to mitigate the toxic effect of Ni by providing buffering action besides enrichment of organic fraction.

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