EFFECT OF ORGANIC AMENDMENTS AND INCUBATION TIME ON EXTRACTABILITY OF Ni AND OTHER METALS FROM CONTAMINATED SOILS

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We evaluated four organic amendments for their effect on AB-DTPA extractable Ni with time in an incubation study. Organic amendments viz. farm yard manure (FM), poultry manure (PM), press mud (PrM) and activated carbon (AC) were applied onto soil @ 2 and 4 % on air-dry weight basis. Soil samples were taken after 30- and 60-days incubation. Soil-applied amendments differed significantly for soil $pH_{1:10}$, OM, AB-DTPA extractable Ni and other metals like Cu, Zn, Mn and Cd. Amendments increased OM in post-incubation soil and increase was maximum was with AC_4 (AC @ 4 %) after both periods. Incubation time decreased OM, decrease being maximum (41 %) and minimum (5 %) with FM_4 (FM @ 4 %) and PrM_2 (PrM @ 2 %), respectively. Maximum pH was with AC_4 and AC_2 (AC @ 2 %) while it was minimum with PrM_4 (PrM @ 4 %). The FM and AC decreased Ni in soil after 30-days incubation but this effect diminished after 60-days incubation. In general, Ni and other metals decreased in soil with time.
Keywords: Organic amendments, metals, incubation, extractability

INTRODUCTION

Nickel contamination of soils is a widespread problem. It is contributed by several anthropogenic and natural sources. Extractability and phytoavailability of Ni and other metals in soils depends on several soil properties like pH, CEC, clay contents, $CaCO_3$ and OM. Organic matter is important soil constituent influencing physico-chemical and biological properties of soils. It reacts strongly with metals in soils; however, its transformations with time could modify its impact on metal behavior in soils. Phytoavailability of Ni and other metals is related to their residence time in soils (Pedersen *et al.*, 2000; Joner and Leyval, 2001). Nickel phytoavailability decreases with increasing its residence time in soils (McLaughlin, 2001). Metals' availability in soils decreased with time due to different reactions like complexation, adsorption and precipitation of metals in soils. The OM could influence these reactions and thus metal retention in soils. Transformations of OM with time could alter its interaction with metals and soils. Limited research work is reported about the effect of OM transformations on metals extractability and phytoavailability in soils. The present study was conducted to monitor the behavior of OM in soils with time and its impact on extractability of Ni and other metals.

MATERIALS AND METHODS

Soil and amendments collection

Soil was collected from an agricultural field irrigated with raw sewage at village 217/RB, Kajlianwala, Faisalabad. Bulk soil was collected from surface (0-15 cm) and transported to green house for experimentation. The FM and PM were collected in bulk from the dairy and poultry farms, University of Agriculture, Faisalabad, respectively. The PrM was collected in bulk from Crescent Sugar Mills, Ltd., Faisalabad and AC was purchased from a scientific store.

Preparation of soil and amendments

Bulk soil was air dried, ground with wooden roller and passed through 2 mm sieve. Soil was artificially contaminated with $Ni(NO_3)_2.6H_2O$ salt solution to achieve 90 mg Ni kg^{-1} soil. After contamination, soil was placed in plastic lined tubs and was wetted to about saturation and allowed to equilibrate for two weeks. On drying, soil was again ground, remixed thoroughly and allowed to equilibrate for further two weeks after wetting it to about saturation. Amendments were air-dried and ground to pass through 2 mm sieve except AC which was already in powder form.

Characterization of soil and amendments

Physico-chemical properties of soil like pH_s, $pH_{1:10}$, EC_e, OM, $CaCO_3$ and soil texture were determined following methods described by the US Salinity Lab. Staff (1954) and Page *et al.* (1982). Organic matter from soil was determined by Walkley-Black method (Jackson, 1962). At the termination of 4 weeks equilibration period, soil sample was extracted with AB-DTPA solution to determine Ni and other metals from contaminated soil. The metals in AB-DTPA extract of soil were determined with atomic absorption spectrophotometer (Thermo S-Series). Amendments were digested in di-acid (HNO_3:$HClO_4$) to determine total metal contents. Metal contents in amendment digests were determined with atomic absorption spectrophotometer. The pH and EC of amendments were measured with pH (Senso Direct 100) and EC (TOA) meters by preparing a slurry of amendments with distilled water (1:10, amendment water ratio). Salient chemical and physical properties of soil and amendments are given in Table 1.

RESULTS

OM contents of post-incubation soil

Organic matter increased significantly (P<0.05) with amendments after 30-days incubation (Fig.1). The maximum OM was recorded with AC_4 (2.73 %) followed by AC_2 (2.47 %) and FM_4 (2.23 %). Similarly, maximum OM in post-incubation soil was observed with AC_4 (1.83 %) followed by PRM_4 (1.72 %) and PM_4 (1.63 %) after 60-days incubation with non-significant differences among treatments. Organic matter decreased with incubation time, decrease being maximum with FM_4 (41%) followed by control (39%) and AC_2 (38%).

Table 1. Characteristics of soil and amendments used in the experiment

Property	Unit	Soil	Organic amendments			
			FM	PM	PrM	AC
Texture	-	Sandy clay loam	-	-	-	-
^1pH_s	-	8.16	-	-	-	-
$^2pH_{1:10}$	-	8.67	7.75	6.99	7.24	10.65
EC	dS m^{-1}	3.50	7.98	7.29	3.82	0.62
SAR		16.00	-	-	-	-
CEC	$cmol_c$ kg^{-1}	6.15	-	-	-	-
OM	%	0.82	59	47	66	38
$CaCO_3$	%	1.78	-	-	-	-
Ni	^{3}mg kg^{-1}	45.06	55	50	43	37
Cu	-do-	3.75	482	407	344	177
Zn	-do-	3.37	240	794	322	87
Mn	-do-	4.01	136	596	346	174

1. pH_s: pH of soil saturated paste extract
2. $pH_{1:10}$: pH of soil suspension (1:10 soil water ratio)
3. AB-DTPA extractable metal concentration in soil and total metal concentration in amendments.

Experimental

The study was conducted in the wire house of the Institute of Soil and Environmental Sciences, University of Agriculture, Faisalabad, having glass roof and open sides. Four organic amendments viz. FM, PM, PrM or AC was applied @ 2 & 4 % onto contaminated soil on air-dry weight basis and mixed thoroughly with soil. The description of experimental treatments is as; FM_4 (FM @ 4 %), FM_2 (FM @ 2 %), PM_4 (PM @ 4 %), PM_2 (PM @ 2 %), PrM_4 (PrM @ 4 %), PrM_2 (PrM @ 2 %), AC_4 (AC @ 4 %), AC_2 (AC @ 2 %). Soil was wetted with distilled water to about saturation and subsequently soil moisture was maintained at about field capacity. Soil samples were drawn at two time intervals, i.e. after 30- and 60-days incubation. Post-incubation soil samples were air-dried, ground with wooden roller and passed through 2 mm sieve. Soil samples were extracted with AB-DTPA solution to determine Ni and other metals (Mn, Zn, Cu, Pb and Cd). The data collected were subjected to ANOVA and means were separated with LSD test using Statistix (Version 8.1).

$pH_{1:10}$ of post-incubation soil

Organic amendments differed significantly (P<0.05) for $pH_{1:10}$ both after 30- and 60-days incubation (Fig. 2). After 30-days incubation, $pH_{1:10}$ was maximum (8.66) with PM_2 followed by AC_2 (8.61) and FM_2 (8.60), while it was minimum with PrM_4 (8.46). After 60-days incubation, maximum pH was recorded with AC_2 (8.62) followed by AC_4 (8.48) while minimum pH was observed with PrM_4 (8.41). The decrease in $pH_{1:10}$ was recorded with incubation time.

AB-DTPA extractable Ni and other metals

Amendments significantly (P<0.05) affected AB-DTPA extractable Ni in soil after 30-days incubation (Fig 3). The PM_4 contained maximum Ni (38 mg kg^{-1}) while it was minimum (23.51 mg kg^{-1}) with PrM_4. The PM_4

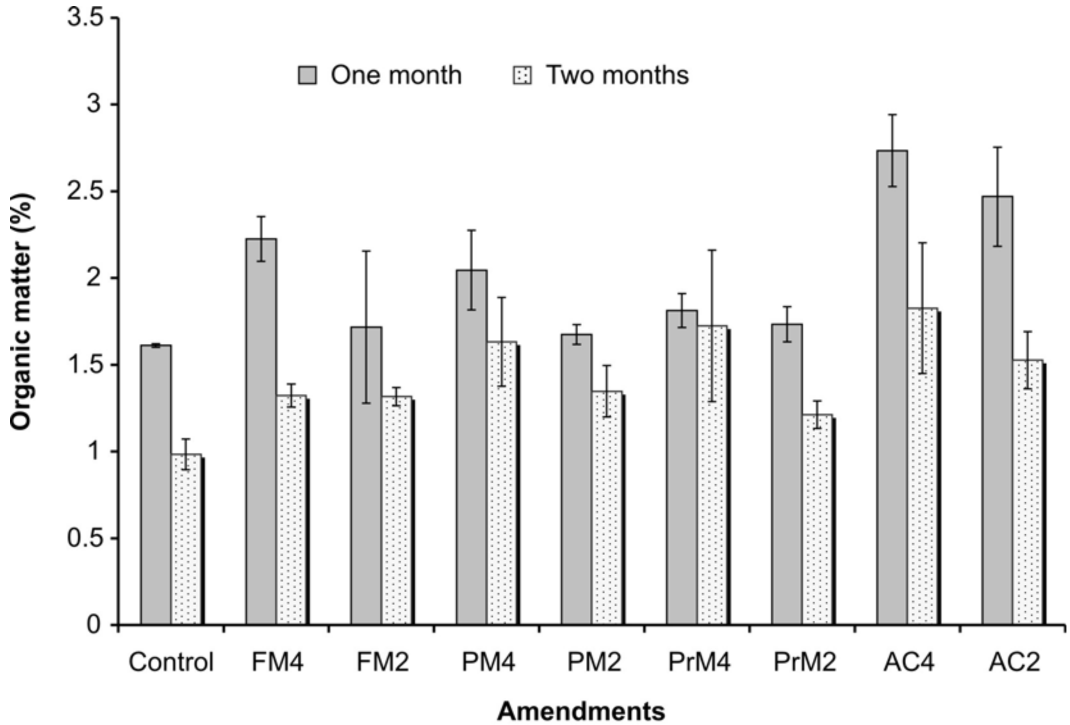

Fig. 1. Effect of amendments on OM of soil after 30- and 60-days incubation

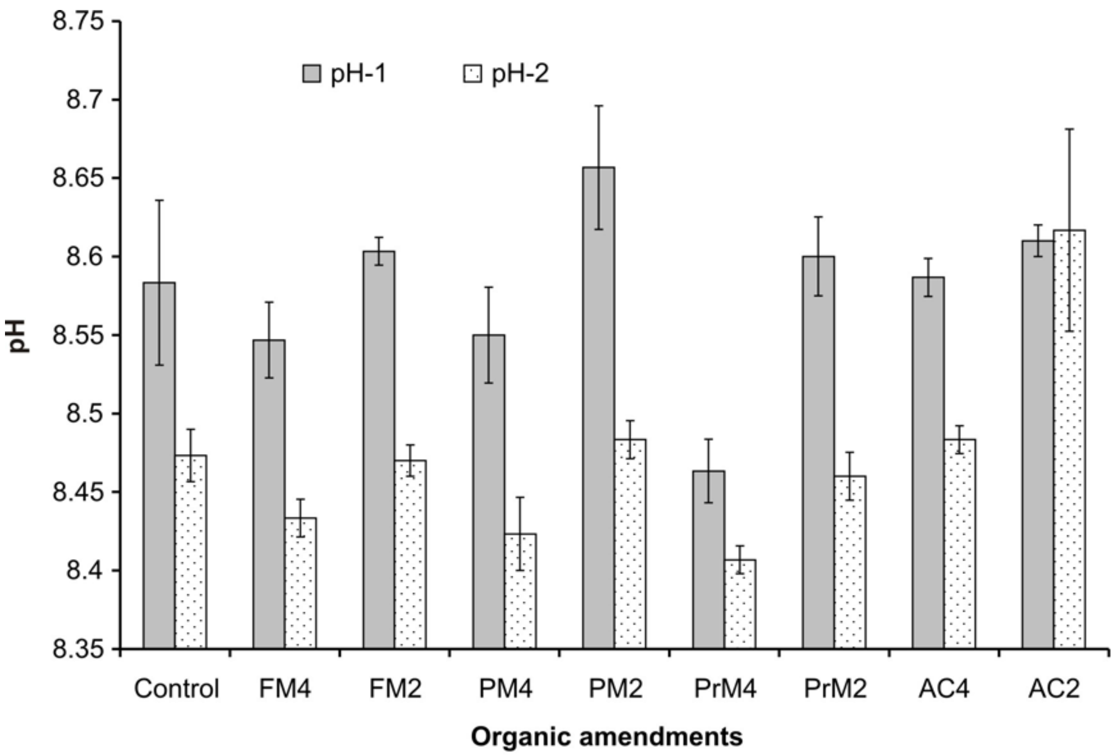

Fig. 2. Effect of amendments on $pH_{1:10}$ of soil after 30- and 60-days incubation

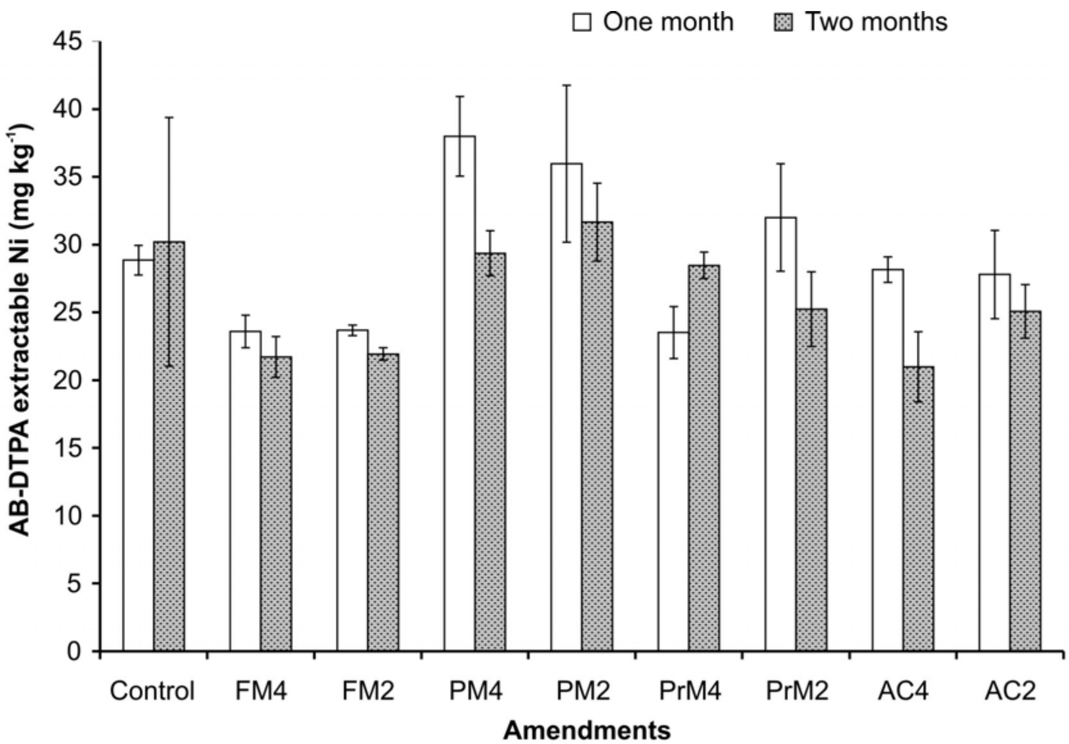

Fig. 3. Effect of amendments on AB-DTPA extractable Ni in soil after 30- and 60-days incubation

increased Ni by 32 % followed by PM_2 (25 %) and PrM_2 (11 %) over that of control. After 60-days incubation, amendments differed significantly ($P<0.05$) for Ni in soil. The PM_2 contained maximum Ni (31.66 mg kg^{-1}) followed by PM_4 (29.37 mg kg^{-1}). Incubation time decreased Ni in soil, decrease being maximum (26 %) with AC_4 and minimum with FM_2 (7 %) over that of control.

After both incubation periods, amendments significantly ($P<0.001$) increased AB-DTPA extractable Mn compared with that of control except AC_4 and AC_2 (Table 2). The PM_2 contained maximum Mn (46.65 & 38.42 mg kg^{-1}) in soil after both incubation periods. After 30-days incubation, Mn was minimum with AC_4 (12.01 mg kg^{-1}) followed by AC_2 (16.23 mg kg^{-1}). The increase in Mn was maximum with PM_2 (181 & 138 %) after both periods of incubation, respectively, compared with that of control. The AC_4 decreased Mn in soil by 28 % over that of control after 30-days incubation. The incubation time decreased Mn concentration in soil due to application of amendments and decrease was maximum with PrM_2 (28 %).

There were highly significant ($P<0.001$) differences among amendments for AB-DTPA-extractable Cu after the both incubation periods (Table 2). Amendments increased Cu in soil except AC_4 and AC_2 after 30-days incubation. The PrM_4 increased Cu by 75 % followed by PM_4 (60 %) compared with that of control. The AC_4 and AC_2 decreased Cu by 19 and 4 %, respectively over that of control. Similarly, after 60-days incubation, increase in Cu was maximum with PM_4 (44 %) followed by PM_2 (42 %) and PrM_4 (26 %) over that of control. After 60-days incubation, AC_4 and AC_2 decreased Cu by 7 and 9 %, respectively, compared with that of control. Incubation time decreased Cu by 31 % due to PrM_4 while increased it with AC_4 and FM_2 by 11 and 6 %, respectively.

Amendments significantly ($P<0.001$) increased AB-DTPA extractable Zn in soil after both periods of incubation except AC_4 and AC_2 (Table 3). After 30-days incubation, PrM_4 contained maximum Zn (48.40 mg kg^{-1}) followed by PM_4 (34.69 mg kg^{-1}). Amendments increased Zn in soil except AC_4 and AC_2 compared with that of control. The AC_4 and AC_2 decreased Zn in soil by 23 and 18 %, respectively, compared with that of control. After 60-days incubation, PM_4 increased AB-DTPA Zn by 316 % followed by PM_2 (177 %) and PrM_4 (69 %) compared with that of control. The Zn decreased in soil with incubation and decrease was maximum with PrM_4 (86%) followed by PrM_2 (68%) and FM_4 (63%) over that of control.

There was a significant decrease in AB-DTPA extractable Cd due to application of amendments after 30-days incubation except PM_4 and PM_2 (Table 3). The

Table 2. Effect of amendments on AB-DTPA extractable concentration (mg kg^{-1}) of Mn and Cu in post-incubation soil

Treatment	Mn (mg kg^{-1})		Cu (mg kg^{-1})	
	30-days	60-days	30-days	60-days
Control	16.63 DE	16.14 E	4.06 DEF	3.92 D
FM_4	34.80 B (+109)	34.94 AB (+116)	5.08 BCDE (+25)	4.49 C (+15)
FM_2	29.99 BC (+ 80)	29.36 C (+ 82)	4.11 CDEF (+ 1)	4.35 C (+11)
PM_4	45.39 A (+173)	36.19 A (+124)	6.48 AB (+60)	5.64 A (+44)
PM_2	46.65 A (+181)	38.42 A (+138)	5.44 BCD (+34)	5.56 A (+42)
PrM_4	23.59 CD (+ 42)	30.63 BC (+ 90)	7.10 A (+75)	4.93 B (+26)
PrM_2	32.09 BC (+ 93)	23.02 D (+ 43)	5.51 BC (+36)	4.31 C (+10)
AC_4	12.01 E (– 28)	11.89 E (– 26)	3.27 F (–19)	3.64 E (– 7)
AC_2	16.23 DE (– 2)	11.92 E (– 26)	3.91 EF (– 4)	3.57 E (– 9)
LSD	9.59**	5.24**	1.44**	0.27**

Figures in columns sharing same letters are statistically non-significant.
Figures in parenthesis are percent decrease (-) or increase (+) over control

Table 3. Effect of amendments on AB-DTPA extractable concentration (mg kg^{-1}) of Zn and Cd in post-incubation soil

Treatments	Zn		Cd	
	Incubation period		Incubation period	
	30-days	60-days	30-days	60-days
Control	7.52 B	3.93 DE	0.12 BC	0.01 C
FM_4	13.66 B (+ 82)	5.08 D (+ 29)	0.10 C (–13)	0.01 C (+ 1)
FM_2	12.81 B (+ 71)	4.81 D (+ 22)	0.10 C (–15)	0.09 B (+1133)
PM_4	34.69 A (+362)	16.35 A (+316)	0.27 A (+131)	0.17 A (+2088)
PM_2	12.91 B (+ 72)	10.86 B (+177)	0.16 B (+939)	0.10 B (+1257)
PrM_4	48.40 A (+544)	6.63 C (+ 69)	0.10 C (–17)	0.06 BC (+ 639)
rM_2	15.92 B (+ 12)	5.09 D (+ 30)	0.09 C (–22)	0.07 B (+ 854)
AC_4	8.91 B (+ 19)	3.04 E (– 23)	0.07 C (–39)	0.05 BC (+ 620)
AC_2	4.04 B (– 46)	3.23 E (– 18)	0.09 C (–26)	0.06 B (+ 734)
LSD	15.21**	1.29**	0.06**	0.06**

Figures in columns sharing same letters are statistically non-significant.
Figures in parenthesis are percent decrease (-) or increase (+) over control

decrease was the maximum (39 %) with AC_4 followed by AC_2 (25.50 %). The PM_4 and PM_2 increased Cd in soil by 130 and 38 %, respectively, compared with that of control. After 60-days incubation, PM_4 increased Cd by 22-fold followed by PM_2 (14-fold) and FM_2 (12-fold) compared with that of control. The incubation decreased Cd in soil, decrease being maximum with control (93%) followed by FM_4 (92%) and PrM_4 (41%).

DISCUSSION

Soil-applied organic amendments significantly affected soil pH, OM and AB-DTPA extractable Ni and other metals in soil. The increase in OM was maximum with AC_4 after both periods of incubation compared with that of other amendments. It indicated that AC contributed stable OM that decomposed slowly with time and thus persist in soil for longer period. Although, PrM contained higher OM compared with that of other amendments (Table 1) but it did not increase OM to greater extent. It could be due to presence of soluble organic compounds that mineralized with time and thus contributed less OM at the end of 60-days incubation. However, decrease in OM content varied with amendments which could be attributed to varying stability of OM contributed by amendments (Walker *et al.*, 2003; Karaca, 2004). Clemente and Bernal (2006) observed a decrease in OM due to its decomposition and it was higher in manure treated soil compared with of compost treated soil.

Amendments significantly affected soil pH after 30-days incubation and non-significantly after 60-days incubation. After 30-days incubation, decrease was maximum with PrM_4 (1.40 %) while PM_2 caused maximum increase in it after 30-days incubation. The AC_2 caused maximum increase in soil pH after 60-days incubation and it could be attributed to high pH of AC (10.65) compared with that of other amendments. The FM had maximum pH next to AC but its effect on soil pH was not pronounced. Similar results were also reported by Walker *et al.* (2003) who reported an increase in soil pH with application of manure and compost which was attributed to high pH of added amendments.

Amendments significantly affected AB-DTPA extractable Ni and other metals after incubation. The FM_2 and FM_4 decreased Ni after 30-days incubation but increased it after 60-days incubation compared with of control. The AB-DTPA extractable Ni decreased after 60-days incubation, decrease being maximum with AC_4. It could be due to its effect on soil pH as it affected maximum increase in pH. High pH could decrease Ni through inducing its precipitation as insoluble inorganic compounds. Karaca (2004) observed that DTPA extractable Ni decreased with application of mushroom compost and grape marc, while tobacco dust increased it after six-month incubation over that of control. Halim *et al.* (2003) recorded a decrease in DTPA-Ni with incubation time and attributed it to its immobilization with humified OM in soil.

Organic amendments affected extractability of other metals (Cu, Mn, Zn, Cd, Pb) in post-incubation soil. Organic amendments significantly affected AB-DTPA extractable Cu in post-incubation soil. Amendments decreased AB-DTPA Cu with incubation time except FM_2 and PM_2. The decrease in Cu with incubation could be due to the conversion of OM into stable form that could bind more Cu. The soil-applied amendments decreased AB-DTPA extractable Zn in soil. Shuman (1999) observed that Zn retention by soil increased in presence of organic materials except poultry litter. In the present study, AB-DTPA extractable Zn decreased with all the amendments. The Zn could precipitate as inorganic compounds during mineralization of organic amendments (Walker *et al.*, 2003) and as $ZnCO_3$ in calcareous soils (Usman *et al.*, 2004). Amendments decreased AB-DTPA extractable Cd in soil with incubation time. Decrease in DTPA-extractable Cd with incubation was also recorded by Karaca (2004) with the application of mushroom compost and grape marc. Decrease in AB-DTPA extractable Cd could be due to high CEC of OM and its ability to complex Cd in the soil.

CONCLUSION

Organic amendments significantly differed for their effect on soil pH, OM, AB-DTPA extractable Ni and other metals due to different chemical properties of amendments applied, nature and amount of OM contributed by these amendments. The AC decreased extractability of Ni and some other metals in soil compared with that of control and other amendments. This might be due to adsorption of Ni on surface of AC that provides large surface area. It could be inferred that organic amendments could be applied to soil for immobilization of Ni and other metals. However, quality of organic amendments applied in terms of their metal contents must be considered.

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