



Full Length Article

Comparative Effect of Activated Carbon, Pressmud and Poultry Manure on Immobilization and Concentration of Metals in Maize (*Zea mays*) Grown on Contaminated Soil

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Abstract

Metal contamination of the soils is a widespread problem and immobilization of metals with organic amendments is one of the different remediation technologies. We investigated the effect of activated carbon, poultry manure and pressmud on immobilization of nickel, manganese, copper, zinc, iron and lead in the contaminated soil, plant growth and metal concentrations in maize shoots. The amendments were applied to the soil at the rate of 4% on dry weight basis. Amendments significantly ($P < 0.001$) affected shoot dry weight and concentrations of all metals in maize shoots as compared to the control. The maximum shoot dry weight (4.54 g pot⁻¹) was recorded with pressmud, while it was minimum with the control (2.22 g pot⁻¹). Maize shoots contained the minimum nickel (3.54 mg kg⁻¹) with activated carbon and the minimum concentrations of manganese (11.02 mg kg⁻¹), zinc (48.06 mg kg⁻¹) and iron (104.66 mg kg⁻¹) were recorded with pressmud. Maize shoots contained the minimum concentrations of copper (25.41 mg kg⁻¹) and lead (53.40 mg kg⁻¹) with poultry manure and control, respectively. Amendments significantly ($P < 0.001$) decreased ammonium bicarbonate-diethylene triamine penta acetic acid (AB-DTPA) extractable concentrations of metals except lead. Activated carbon treated pots had minimum AB-DTPA extractable concentrations of all the metals except iron and lead. Activated carbon was most effective in immobilization of Ni, Mn, Zn and Cu decreasing AB-DTPA extractable Ni in the soil, while Fe and Pb was increased due to application of other amendments. © 2013 Friends Science Publishers

Keywords: Amendments; Metals; Immobilization; Concentration; Maize

Introduction

Agriculture in Pakistan is confronted with shortage of good quality irrigation water due to arid and semi-arid climatic conditions (Ghafoor *et al.*, 2002). Shortage of good quality water for irrigation is the major factor that compels the farmers to use other sources of irrigation to realize the yield potential of the field crops. Among the alternate sources of irrigation, raw city effluent is a potential source, which is a common choice of farmers in peri-urban areas due to its sustainable supply and nutrient enrichment (Ghafoor, 2004; Ensink *et al.*, 2004). Raw city effluent is a mixture of industrial effluent and domestic waste, due to which it contains heavy metals particularly Ni which are persistent and non-biodegradable in nature. Use of metal contaminated raw city effluent resulted in the contamination of soil with metals and thus could pose different environmental and health problems (Mapanda *et al.*, 2005). Average concentration of Ni in earth crust and agricultural soils is 75 and 40 mg kg⁻¹, respectively which could reach up

to > 10000 mg kg⁻¹ in the soils which are developed from ultramafic parent material (Alloway, 1990).

Essentiality of Ni is now well established for higher plants, however its higher concentration could be toxic to the plants (Farago and Cole, 1988) and could modify different physiological/biochemical processes (Morgutti *et al.*, 1984; Jones and Hutchinson, 1988; Pandolfini *et al.*, 1992; Seregin and Kozhevnikova, 2006). Nickel toxicity decreases membrane permeability due to higher extracellular peroxidase activity (Pandolfini *et al.*, 1992). Nickel causes skin allergy, hypersensitivity in occupationally exposed persons and is haematotoxic, immunotoxic, reproductive toxic and carcinogenic agent (Das *et al.*, 2008).

Nickel contaminated soils could be used safely for agricultural purpose by adopting different management options. Management strategy, which takes care of different ecological risk and human health, could be the best option (ATSDR, 2005; Demir *et al.*, 2005). Recently, environmentally friendly techniques which avoid excavation

and environmental disturbances are preferred over the other techniques. Among different management strategies, immobilization of Ni and other metals with the soil applied amendments is safe and environmentally friendly approach. In-solubilization of Ni and other metals remediate toxic effects on living organisms. Conventionally, amendments containing lime and organic matter are applied to the soils for in-situ immobilization of Ni and other metals in soils. Application of organic amendments for metal immobilization is important due to beneficial effects on physico-chemical properties of soil (Karaca, 2004). Different soil and plant factors like soil pH, cation exchange capacity, organic matter (OM) contents, CaCO₃, nutrient status of soils and plant species, controls the phytoavailability of metals in the soils (Seregin and Kozhevnikova, 2006). OM is the most important due to its effect on behavior of different metals including Ni in the soil which controls availability of Ni and other metals.

Organic matter could form chelates of various stabilities, which control mobility and accumulation of Ni and other metals in the soil (Stevenson and Cole, 1999). Nature and type of organic matter influenced immobilization of metals in the soil and ultimately their environmental fate in the soil (Sabir *et al.*, 2008). Organic amendments are conventionally used for immobilization of metals in the soil but Activated carbon is new addition to these amendments. Activated carbon (AC) is a carbon containing material having excellent capacity to adsorb metals due to large surface area and adsorption capacity (Lima and Marshall, 2005; Ucer *et al.*, 2006). Lyubchik *et al.* (2008) reported that metal removal with AC was very effective and 50-55% of total removal of metals could be due to metal hydroxide precipitation and 15-20% could be due to metal cation adsorption on negatively charged surface of AC. Activated carbon is generally used for removal of metals from wastewater but its use to immobilize metals from soils is rare and thus needs to be investigated. The present study was planned to investigate and compare the effect of AC, pressmud (PrM) and poultry manure (PM) on immobilization of nickel (Ni), manganese (Mn), copper (Cu), zinc (Zn), iron (Fe) and lead (Pb) and their concentrations in maize shoots (*Zea mays* L.)

Materials and Methods

Soil Collection and Preparation

Bulk soil was collected from the field being irrigated with raw city effluent in suburban areas of Faisalabad. The soil is relatively young carrying negligible pH dependent negative charge and dominantly contains illite (McNeal, 1966; Ranjha *et al.*, 1993). This soil is developed from alluvial parent material transported from the Himalayas by River Indus (Riaz-ul-Amin, 1986). The soil was air-dried before grinding with wooden roller to pass through 2 mm sieve and analyzed for saturated paste pH (pHs), electrical

conductivity of saturated paste extract (EC_e), organic matter (OM), lime contents (CaCO₃), soil texture and cation exchange capacity (CEC) following appropriate methods (US Salinity Lab. Staff, 1954) and Page *et al.* (1982) (Table 1). The concentration of ammonium bicarbonate-diethylene triamine penta acetic acid (AB-DTPA) extractable metals (Ni, Mn, Zn, Cu, Fe and Pb) were determined with atomic absorption spectrophotometer (Thermo S-Series, Thermo-electron) following Soltanpour (1985). Soil was impregnated with Ni by spraying solution of Ni(NO₃)₂·6H₂O to the soil to achieve 90 mg Ni kg⁻¹ soil. The impregnated soil was mixed uniformly and thoroughly to get homogeneity and then subjected to alternated cycle of wetting and drying for four weeks. After alternate wetting and drying, dried soil was again ground, mixed thoroughly and appropriate sample was taken to determine AB-DTPA extractable metals.

Amendment Collection and Preparation

Poultry manure, PrM and AC was obtained from the poultry farm, University of Agriculture, Faisalabad, Crescent Sugar Mills Ltd., Faisalabad and scientific supplier, respectively. Air-dried PM and PrM were ground to pass through 2 mm sieve, while AC was originally in powdered form. Amendments were analyzed to determine different physico-chemical properties, which are given in Table 1.

Pot Experiment

The experiment was conducted in the rain-protected wire house of the Institute of Soil and Environmental Sciences, University of Agriculture, Faisalabad during 2008. Experiment was conducted in glazed pots with 10 kg soil in each pot and having no leaching provision. Amendments were thoroughly mixed with the contaminated soil at the rate of 4% on air dry weight basis and filled into the pots. Nitrogen (300 kg ha⁻¹), phosphorus (100 kg ha⁻¹) and potassium (50 kg ha⁻¹) was supplied to the plants through urea, di-ammonium phosphate and potassium sulphate. Ten healthy and uniform sized seeds were sown in each pot and after germination, five maize seedlings were maintained in each pot. Extra seedlings were uprooted and crushed into the same pots. Nitrogen was supplied to the plants in split doses; at the time of sowing and after 25 days of sowing while phosphorus and potassium was applied at the time of sowing. Experimental pots were arranged following completely randomized design (CRD) with three replications. After 50 days of sowing, plants were harvested at about 1 cm above soil surface. Appropriate soil sample was drawn from each pot after plant harvesting to extract AB-DTPA extractable Ni and other metals and ultimately their determination with atomic absorption spectrophotometer (AAS). After harvesting, plants were rinsed with 1% HCl, tap water and distilled water in sequence to clean atmospherically deposited contamination from plants. Air-dried plant samples were dried at 65±5°C

in oven to constant weight. Oven-dried plant material was finely ground with a mechanical grinder (MF 10 IKA, Werke, Germany) to pass through 1 mm sieve. Ground plant sample (0.5 g) was digested in di-acid mixture (HNO₃ and HClO₄) at 150°C (Miller, 1998). Metal concentrations in digested plant samples and soil extracts were determined with AAS (Thermo S-Series, Thermo-electron).

Statistical Analysis

The data obtained were subjected to statistical analysis using software statistix 8.1 and means were separated from each other following least significant difference (LSD) test.

Results

Plant Growth

Amendments significantly ($P < 0.001$) increased shoot dry weight (SDW) of maize compared to the control (Table 2). Maximum SDW was recorded with PrM (4.54 g pot⁻¹), while it was minimum with control (2.29 g pot⁻¹). Except PrM, SDW was statistically at par with other amendments but significant compared to the control. Pressmud increased SDW to the maximum extent (98%), while the increase was the minimum (15%) with PM as compared to the control. Shoot dry weight of maize decreased with increasing concentration of metals in shoots except Cu and Pb (Fig. 1). Shoot dry weight had significant negative correlations with concentration of Fe ($r = -0.95$, $P < 0.001$, $n = 12$) and Mn ($r = -0.85$, $P < 0.001$, $n = 12$) in maize shoots. Shoot dry weight decreased with increasing concentration of Ni and Zn in shoot, however, correlations between SDW and concentration of these metals were non-significant. Shoot dry weight increased with increasing concentration of Pb and Cu in maize shoot. SDW was significantly correlated with Pb concentration in shoot ($r = 0.70$, $P < 0.05$, $n = 12$) and non-significantly with Cu concentration in shoot.

Metals Concentration in Maize Shoots

Effect of amendments was significant ($P < 0.05$) on Ni concentration in the shoots of maize (Table 2). Poultry manure increased Ni concentration in maize shoots by 3% while other amendments decreased it compared to the control. However, Ni in maize shoots with PM was statistically at par with control. The maximum Ni concentration (7.03 mg kg⁻¹) in maize shoots was recorded with PM and it was minimum (3.54 mg kg⁻¹) with AC. The decrease in Ni concentration in shoots of maize was the maximum with AC (48%) followed by PrM (33%) compared to the control. Amendments significantly ($P < 0.001$) affected Fe concentration in maize shoots compared to the control (Table 2) and the plants grown in PM amended pots had maximum Fe concentration (154 mg kg⁻¹) and those grown in PrM amended pots had the minimum Fe (104 mg kg⁻¹) in their shoots. The Fe

concentration in the shoots of maize plants grown in PrM amended pots was 30% higher than the plants grown in control pots. Amendments significantly ($P < 0.001$) decreased Mn concentration in maize shoots compared to the control plants (Table 2). The plants grown in PrM amended pots contained the minimum Mn concentration (11.02 mg kg⁻¹), while the plants grown in control pots had the maximum Mn concentration (35.60 mg kg⁻¹) in shoots. The application of PrM decreased Mn concentration in maize shoots by 69%, while PM and AC decreased Mn concentration by 39 and 27% compared to the control. Poultry manure significantly ($P < 0.001$) increased Zn concentration in maize shoots while AC and PrM decreased it compared to the control plants (Table 2) The Zn in maize shoots was the maximum (232 mg kg⁻¹) with PM that was 89% higher than the Zn in shoots of control plants. The decrease in Zn concentration with PrM and AC was 61 and 50%, respectively compared to the control. Amendments differed significantly ($P < 0.001$) for Cu concentration in maize shoots (Table 2). The maximum Cu concentration (40.49 mg kg⁻¹) was recorded in shoots of maize plants grown in AC amended pots and it was the minimum (25.42 mg kg⁻¹) in the plants grown in PM amended pots. Poultry manure decreased Cu in shoots of maize by 35% followed by PrM (2%) while AC increased it by 4% compared to the control plants. Amendments significantly ($P < 0.001$) increased Pb in maize shoots compared to the control (Table 2). The maximum Pb concentration (109.45 mg kg⁻¹) was observed in the plants grown in PrM amended pots while it was the minimum (53.4 mg kg⁻¹) with control. Although, all the amendments increased Pb concentration but the increase was minimum (46%) with AC as compared to the control.

AB-DTPA-extractable Metals in the Post-experiment Soil

The AB-DTPA-extractable Ni in the post-experiment soil was affected significantly ($P < 0.001$) due to application of amendments (Table 3). All the amendments increased AB-DTPA extractable Ni in the soil with the exception of AC that decreased Ni by 33% compared to the control. The maximum increase in AB-DTPA-Ni in the soil was recorded with application of PrM which was 47% higher compared to the control. The maximum AB-DTPA Ni concentration (31.72 mg kg⁻¹) in the soil was recorded with PrM followed by PM (29.83 mg kg⁻¹) and it was the minimum (14.35 mg kg⁻¹) with AC. Amendments significantly ($P < 0.001$) increased AB-DTPA extractable Fe in the soil compared to the control (Table 3). The AB-DTPA extractable Fe was the maximum (26.82 mg kg⁻¹) in PM amended pots and it was minimum (8.37 mg kg⁻¹) in the control pots. The increase in AB-DTPA-Fe was the maximum (220%) with PM and it was the minimum with AC (54%) compared to the control. Poultry manure and PrM significantly ($P < 0.001$) increased AB-DTPA extractable Mn, while AC decreased Mn in the soil

Table 1: Physico-chemical properties of the experimental soil and amendments

Characteristic	Unit	Soil	Amendments		
			Pressmud	Poultry Manure	Activated Carbon
Textural class	-	Sandy clay loam			
pH _s		8.16	6.99	7.24	10.65
EC _e	dS m ⁻¹	3.50	7.29	3.82	0.62
SAR	(mmol L ⁻¹) ^{1/2}	16.0	-	-	-
CEC	cmol _c kg ⁻¹	6.15	-	-	-
CaCO ₃	%	1.78	-	-	-
OM	%	0.82	47	66	38
Ni before incubation	mg kg ⁻¹	0.33	49.57	42.66	37.14
Ni after incubation	mg kg ⁻¹	45.0			
Zn	mg kg ⁻¹	3.37	794	322	87
Cu	mg kg ⁻¹	3.75	407	344	177
Mn	mg kg ⁻¹	4.01	596	346	174

Table 2: Effect of organic amendments on shoot dry weight (SDW) and metal concentration in maize shoots; (The values are mean ± standard error)

Treatment	SDW (g pot ⁻¹)	Metal concentration (mg kg ⁻¹)					
		Ni	Mn	Cu	Zn	Fe	Pb
Control	2.29 ± 0.28	6.82 ± 0.14	35.59 ± 0.82	39.09 ± 1.25	122.89 ± 4.90	149.25 ± 9.31	53.40 ± 5.70
PM	2.63 ± 0.12	7.03 ± 0.30	21.73 ± 0.51	25.41 ± 2.53	232.25 ± 10.21	154.54 ± 0.63	89.96 ± 4.56
PrM	4.54 ± 0.16	4.58 ± 0.28	11.02 ± 0.80	38.15 ± 0.93	48.06 ± 0.32	104.66 ± 2.45	109.45 ± 4.93
AC	2.81 ± 0.37	3.54 ± 0.45	26.08 ± 2.52	40.49 ± 0.62	61.26 ± 18.79	147.73 ± 5.38	77.86 ± 5.57
LSD	0.82***	1.02***	4.59***	4.96***	35.79***	18.60***	16.99***

Where, as PM (poultry manure); PrM (pressmud); AC (activated carbon); *** indicate highly significant differences at P < 0.001

Table 3: Effect of organic amendments on ABDTPA extractable metal concentration in post-experiment soil; The values are mean ± standard error

Treatment	Metal concentration (mg kg ⁻¹)					
	Ni	Mn	Cu	Zn	Fe	Pb
Control	21.52 ± 0.27	7.70 ± 0.16	4.20 ± 0.18	4.60 ± 0.13	8.37 ± 0.57	4.21 ± 0.05
PM	29.83 ± 1.13	12.73 ± 0.28	4.80 ± 0.02	17.59 ± 1.00	26.82 ± 3.32	4.49 ± 0.07
PrM	31.72 ± 0.56	8.71 ± 0.58	4.81 ± 0.15	8.02 ± 0.29	14.26 ± 0.56	4.53 ± 0.13
AC	14.35 ± 0.43	4.66 ± 0.36	3.33 ± 0.18	3.95 ± 0.10	12.85 ± 1.10	4.37 ± 0.15
LSD	2.22***	1.23***	0.48***	1.73***	5.85***	0.33ns

Where, as PM (poultry manure); PrM (pressmud); AC (activated carbon); *** indicate highly significant differences at P < 0.001, ns is non-significant

compared to the control. The maximum Mn concentration (12.73 mg kg⁻¹) in the soil was recorded with PM and it was the minimum (4.66 mg kg⁻¹) with AC (Table 3). Poultry manure increased the AB-DTPA-Mn by 65 % while AC decreased it by 40% compared to the control. In case of Zn, all amendments increased AB-DTPA Zn in the soil except AC that decreased its concentration by 14% compared to the control (Table 3). The AB-DTPA Zn was the maximum (17.59 mg kg⁻¹) in the pots amended with PM, while it was the minimum (3.95 mg kg⁻¹) in AC amended soils. Activated carbon significantly (P < 0.001) decreased AB-DTPA extractable Cu in the soil while PM and PrM increased Cu in the soil compared to the control (Table 3). The maximum AB-DTPA-Cu concentration (4.81 mg kg⁻¹) in the soil was recorded with PrM followed by PM (4.80 mg kg⁻¹) and it was the minimum (3.33 mg kg⁻¹) with AC. The effect of amendments was non-significant on AB-DTPA extractable Pb in the soil, however all the amendments increased Pb in the soil compared to the control (Table 3). The increase was the minimum with AC (4%) and maximum with PrM (7%) compared to the control.

Discussion

All the amendments significantly increased SDW of maize compared with that of the control. Higher biomass production with organic amendments compared to the control in contaminated soils could be due to supplemental supply of nutrients particularly nitrogen released during decomposition of organic amendments (Clemente *et al.*, 2007). The plants grown in PrM amended pots produced the maximum SDW. This could be due to its higher OM contents, which on mineralization can supply additional nutrients, improve buffering capacity and enhance nutrient cycling and thus can improve plant growth (Stewart *et al.*, 2000; Clemente *et al.*, 2007). Activated carbon decreased Ni concentration in maize shoots while PrM and PM increased it compared to the control. This could be due to the immobilization of Ni with AC in the soil compared to other amendments as evidenced from less AB-DTPA-Ni in AC amended pots (Table 3). The decrease in Ni in wheat shoots due to decrease in DTPA extractable Ni has been reported by Arensen and Singh (1998). Amendments decreased the

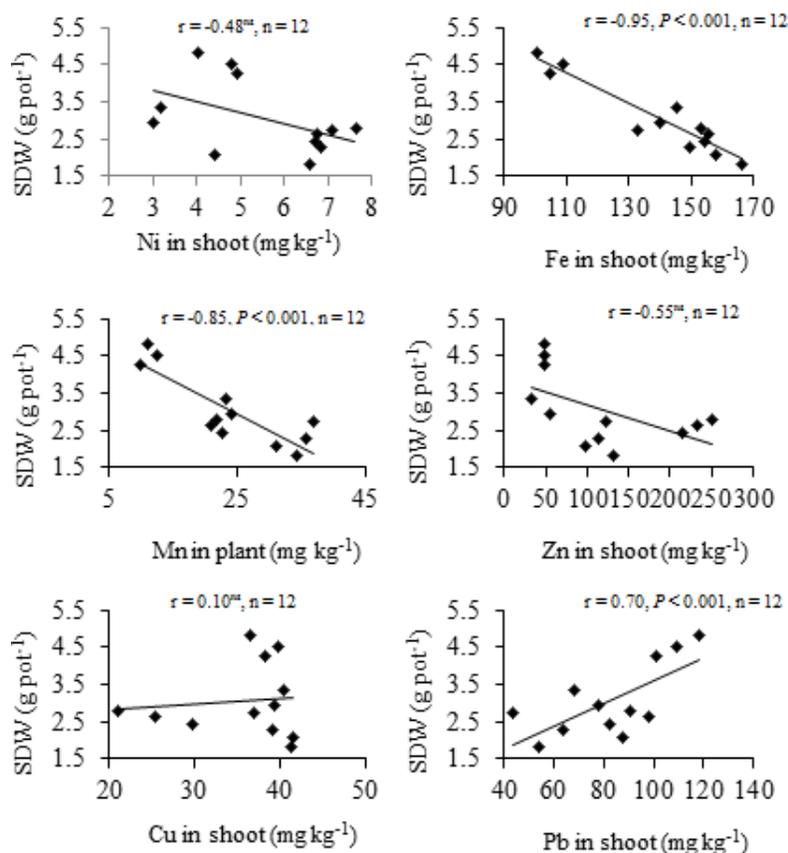


Fig. 1: Correlation between between shoot dry weight of maize and concentration of metals in maize shoots

Mn concentration in shoots of maize plants compared to the control plants and the decrease was the maximum with PrM. This differential effect of amendments may be due to different nature and amount of OM and pH of amendments applied (Chamon *et al.*, 2005). The Zn concentration was the maximum in shoots of maize plants grown in PM amended, which could be due to higher contents of Zn (Table 1) in this amendment that caused higher AB-DTPA extractable Zn in the soil (Table 3) and thus its preferred absorption by maize plants. Activated carbon decreased AB-DTPA extractable Ni in the soil and this could be due to high pH (10.6) of AC (Table 1) compared to other amendments that might cause precipitation of Ni in soil. The strong complexation of Ni with humified OM in AC could decrease AB-DTPA extractable Ni in the soils (Narwal and Singh, 1998; Misra and Chaturvedi, 2007). Organic matter might have re-distributed available Ni to the fractions associated with OM and other components of the soil (Karaca, 2004). Higher concentration of Mn in PM amended pots could be due to the higher contents of Mn in PM inherently (Table 1). Lower concentration of Mn in AC amended pots could be to high pH of AC that could have immobilized Mn and this differential response of AC may be due to its high pH and OM contents (Chamon *et al.*, 2005).

In conclusion, effect of amendments was significant on SDW, concentration of metals in maize shoots and AB-DTPA extractable metals in the post-experiment soil. Maize produced maximum SDW with PrM application. Activated carbon was most effective in immobilization of Ni, Mn, Zn and Cu, thus decreasing their AB-DTPA extractable concentration in the soil while Fe and Pb was increased due to application of all amendments. Activated carbon decreased concentration of Ni and Pb in maize shoots to maximum extent compared to control, while PrM was most effective in decreasing the concentrations of Fe, Zn and Mn in maize shoots compared to control.

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(Received 12 October 2012; Accepted 14 January 2013)