INFLUENCE OF FARMYARD MANURE ON RETENTION AND AVAILABILITY OF NICKEL, ZINC AND LEAD IN METAL-CONTAMINATED CALCAREOUS LOAM SOILS

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Abstract. Continuous irrigation of soils with untreated effluents can result in the accumulation and translocation of some metals in the soils and plants. Application of farmyard manure (FYM) to such soils may increase or decrease their availability and retention time. Calcareous soils contaminated with 100, 200, and 400 mg kg^{-1} Ni, Zn, and Pb as chloride salts were used, and farmyard manure added (40 g kg^{-1} for 90 days) with moisture contents at field capacity. Soil samples were drawn at 30 day intervals, and metals extracted with (AB-DTPA) $C_{14}H_{23}NO_3O_{10}$. With FYM application of 400 mg kg^{-1}, Ni availability increased from 179 (day 30) to 240 mg kg^{-1} (day 90); Zn from 163 (day 30) to 230 mg kg^{-1} (day 90), but, Pb decreased from 214 to 161 mg kg^{-1}. FYM forms multi-dentate complex which greatly enhances the Ni and Zn solubility, and organic matter immobilizes Pb in the soil.

Keywords: availability, nickel, zinc, lead, farmyard manure, contaminated soil.

Introduction

Irrigation with raw city effluents is becoming a major threat to environment sustainability in many of the developing countries. Raw city effluent is taken as a good source of nutrients, however, depending upon its sources; it can introduce many of the heavy metal elements in soils (Murtaza *et al.* 2010). From soil, heavy metals can enter into the food chain through the consumption of contaminated food. Prolonged consumption of such contaminated food could pose severe threat to human health. Therefore, management and remediation of metal contaminated soils are very important for producing safe food from such soils. Remediation or cleaning up of contaminated sites with engineering based technologies requires heavy cost and skilled manpower. Moreover, such technologies are disruptive to site and are not considered as environmentally friendly because of the harsh impact of amendments on site properties. Therefore, it is need of time to identify soil amendments for not only improving soil properties but also restraining the mobility and availability of heavy metals to plants and leaching to ground water.

Phytoavailabilty of metals depend upon physical and chemical characteristics of soil such as pH, redox potential, cation exchange capacity, composition and concentration of organic amendments (Pinto et al.2015). Organic amendments like farmyard manure (FYM), press mud, compost etc. not only improve physical, chemical, biological and fertility property of soils, but can also be employed in altering the availability of metal contaminants in soils. Soil-applied animal manures increased the solubility of metals (Ni, Zn, and Pb) shortly after adding, through the formation of soluble organo-metallic complexes (Almas *et al.* 1999). There is also the possibility that metals become more tightly bound to organic materials, either through diffusion into or through occlusion in organic molecules (Davis 1984). Metals like Zn, Pb, and Ni reacted with soil organic matter by ion exchange, complexation, and precipitation reactions, but complexation reactions are thought to dominate (Clemente *et al.* 2006; Ping *et al.*

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2008). It is well known that the availability of heavy metals decreases with increasing retention of a heavy metal either by silicate clays, calcite, and/or soil organic matter. Such retention of heavy metals is ascribed to reactions between metal ions and soils like adsorption, precipitation, and/or complexation (Alexander 2000; Joner, Leyval 2001; Park *et al.* 2011). According to Walker *et al.* (2003) the retention of metals (i.e. Cu, Zn, Mn, Fe, and Pb) was greater with manure than with compost. On the other hand, the addition of sewage sludge, increased the mobile fraction of Zn, Cd, Cu, and Ni but decreased that of Pb compared to the control treatment (Usman *et al.* 2004). Immobilization of metals by interaction with humic substances could occur through the formation of insoluble complexes or through solid-phase complexation to humates present as coatings on clay surfaces (Stevenson, Cole 1999).

In order to understand the effect of FYM on the availability and retention of heavy metals, detailed information is needed. A large number of studies have been carried out to explore the role of incubation time, type and rate of organic amendments on metal chemical forms and/or fractions in acid and neutral soils (Bataillard *et al.* 2003; Davies *et al.* 2003; Lu *et al.* 2005), however, very little work has been conducted to study the effect of FYM on the availability and retention of heavy metals in calcareous metal contaminated soils. The objective of this study was to understand the effect of FYM on the availability and retention of Ni, Pb, and Zn in metal-contaminated calcareous loam soils at different incubation times.

1. Materials and methods

1.1. Soil sampling and analysis

Soil for the experiment was collected from the plough layer (0–15 cm) in bulk from a field located in the village 199 RB (Rakh Branch) Gattwala, Faisalabad. Soil belongs to Lyallpur soil series (loamy, mixed, hyperthermic Typic

Calci-argids) having geographical coordinate viz. longitude 73°11′06″ and latitude 31°27′08″.

Soil was air-dried, thoroughly mixed, and passed through a 2-mm sieve before analysis. These soil samples were analyzed (Table 1) for pH_s (Jenco pH meter 6718, Taipei Hsien, Taiwan, R.O.C.), electrical conductivity (EC_e) by a conductivity meter (HI 8033, Hanna Instruments, Woonsocket, USA), particle size distribution by the hydrometer method (Bouyoucos 1962), organic carbon by the Walkley-Black wet combustion method (Nelson, Sommers 1982), and lime ($CaCO_3$) by the calcimeter method (Moodie *et al.* 1959).

Metals were extracted with AB-DTPA. The AB-DTPA extracting solution was prepared by dissolving 79.10 g NH_4HCO_3 and 1.97g of DTPA in a liter of solution adjusted to pH 7.6 (Soltanpour 1985). Soil (10 g) was placed in a 250-mL Erlenmeyer flask and 20 mL of freshly prepared extracting solution was added. The mixture was shaken on a reciprocating shaker at 180 cycles per minute by keeping the flasks uncovered at room temperature. According to Soltanpour (1985) the extractable AB-DTPA solution allows the DTPA to chelate and extract metals efficiently from calcareous soils. The concentration of Ni, Zn, and Pb in the filtrate was determined by atomic absorption spectrophotometer (AAS; Thermo S-series, Hitachi, Tokyo, Japan). For artificial spiking of soils, solutions containing 100, 200, and 400 mg kg^{-1} Ni, Zn, and Pb as chloride salts were sprayed onto the soil followed by thorough mixing.

After thoroughly mixing the metal solutions with soil, it was placed in plastic pots (line with polyethylene sheet to check leakage of solution) at 1 kg soil per pot. Soil was equilibrated in a greenhouse at field capacity (moisture content approximately (1/3 bar) equivalent to 50% of the saturation percentage of soil for 35 days). After the 35-day of equilibration period, the soil was air-dried and passed through a 2-mm sieve again. Air-dried FYM (Table 2) collected from a nearby livestock farm was passed through a 2-mm sieve and mixed uniformly with metal contaminated soil in the amount of 40 g kg^{-1} soil. Plastic pots of 2-L capacity containing experimental soil were arranged in triplicate using a completely randomized design

Table 1. Physical and chemical characteristics of soil used in the study

Soil characteristics	Unit	Value
pH_s	–	7.72
EC_e	dS m^{-1}	2.4
Organic matter	g kg^{-1}	5.8
$CaCO_3$	g kg^{-1}	54.7
Clay	g kg^{-1}	240.0
Saturation percentage	%	34.4
Textural class	–	Loam
AB-DTPA extractable metals		
Ni	mg kg^{-1}	0.33
Zn	mg kg^{-1}	3.0
Pb	mg kg^{-1}	2.9

Table 2. Properties of farmyard manure

Property	Unit	Value
Moisture content	g g^{-1}	0.13
pH		7.75
EC (1:10 FYM-water slurry)	dS m^{-1}	7.9
Organic carbon	g kg^{-1}	349
Total N	g kg^{-1}	16.8
Avail. Ni	mg kg^{-1}	0.10
Avail. Zn	mg kg^{-1}	0.19
Avail. Pb	mg kg^{-1}	0.22

and the lids of pots were kept loose to allow gaseous exchange and avoid the build up of CO_2 in pots. A similar set of treatments, but without amendments (control), was kept for comparison.

1.2. Analysis of farmyard manure (FYM)

The water soluble contents of Ni, Pb, and Zn in FYM were determined by preparing slurry with distilled water, i.e., 1:10 (w/v) ratio of FYM to distilled water. The pH and EC were also measured from the FYM-water slurry. The organic matter of FYM was determined by dry ashing while N was determined by the Kjehldal method (Jackson 1962).

1.3. Soil incubation and heavy metals determination

The pots were incubated at room temperature (25±2 °C) and moisture content (0.13 g g^{-1}) was maintained at field capacity throughout the experimentation and adjusted gravimetrically through the addition of distilled water. The soil was incubated for a 90- d period. Soil samples (30 g each) were taken at 30, 60, and 90 days and were extracted with AB-DTPA (Soltanpour 1985). The concentrations of Ni, Zn, and Pb were determined using atomic absorption spectrophotometer (AAS; Thermo S-series, Hitachi, Tokyo, Japan).

1.4. Statistical procedures

The significant differences between concentrations of Ni, Zn, and Pb in soils were assessed by ANOVA (Analysis of Variance) and DMR (Duncan's Multiple Range test) using the M STATC version 1.10 packages (MSTAT; East Lansing, MI.) (Russel, Eisensmith 1983) and statistical differences among treatments were defined at P < 0.05.

2. Results and discussion

2.1. Soil pH

The importance of soil pH on metal availability is well established as it influences the metal adsorption, retention, and transport. Soil pH was significantly affected by FYM and time during the study (Fig. 1). Soil pH decreased by
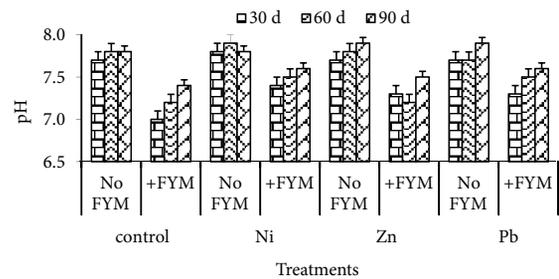

Fig. 1. Effect of FYM addition on soil pH at different incubation times. [FYM – farmyard manure]

the application of FYM. In the control treatment where no FYM was added it was 7.70 at day 30, which decreased to 7.00 by the application of FYM. Soil pH decreased from 7.80 to 7.40 by the application of FYM at day 90 in the control. Its values showed a similar trend for Ni, in the absence of FYM it was 7.80, which decreased to 7.60 with the addition of FYM at day 90. For Zn and Pb the soil pH decreased from 7.90 to 7.50 and 7.90 to 7.60, respectively, with the application of FYM at day 90.

Ostensibly, the decrease in soil pH with FYM application was due to the decomposition of organic matter into humic and fluvic acids, which lower the soil pH (Stevenson, Cole 1999). As soil pH decreases, metals like Ni and Zn must compete with the extra H$^+$ and Al^{3+} for positions on the exchange sites, solubility of these metals increases in the soil solution and a greater proportion is present as highly available free metal ions in the soil solution (McBride 1982; Sauve *et al.* 1997).

2.2. Availability of nickel

Availability of nickel was not significantly affected throughout the study period (Fig. 2). For the control, native Ni was <1 mg kg^{-1} and slight mobilization was observed with FYM at a first sampling time, i.e., at day 30 (1.07 mg kg^{-1}), which became 1.65 mg kg^{-1} at day 90. At 100 mg kg^{-1} Ni application rate, no major change in available Ni was observed without FYM, decreasing from 29.5 mg kg^{-1} on day 30 to 26.8 mg kg^{-1} at day 90. On the other hand, with manure application, the concentration
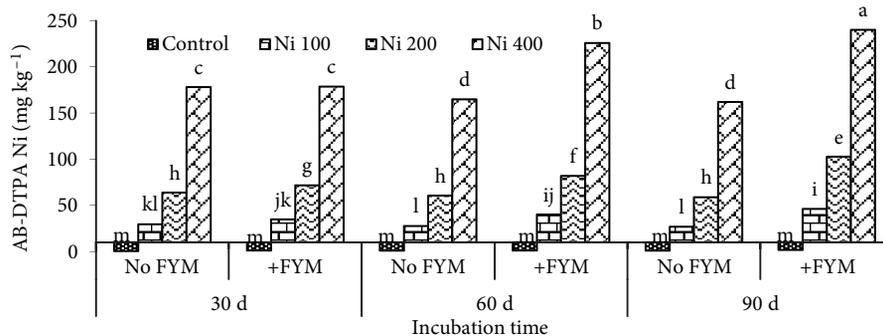

Fig. 2. Effect of incubation time on availability of Ni. FYM – farmyard manure; d – day.
Lower case letters indicate the significance of treatments at P < 0.05

of Ni increased and remained higher than that in the un-amended soil. With FYM addition, 34.8 mg kg^{-1} Ni was in available form at day 30, which increased to 46.2 mg kg^{-1} by the end of the experiment. At 200 and 400 mg kg^{-1} Ni application rates, Ni decreased in unamended soil, whereas manure application increased the Ni concentration. Martinez *et al.* (2003) observed a similar behavior between dissolved organic carbon and soluble Ni concentration in OM-rich soil, i.e., increasing the solubility with incubation time up to 100 days and no further change was observed until the conclusion of the experiment after 600 days. However, the experimental conditions were different as they used natural metal contaminated (Pb 120 mg kg^{-1}, Ni, 800 mg kg^{-1}, and Zn 1480 mg kg^{-1}) silt loam to sandy clay loam acidic grassland soils.

Ostensibly, the increase in available Ni with FYM was due to the formation of soluble Ni-organic complexes from decomposed organic matter (Fig. 2). The addition of FYM to soil results in the increased dissolved organic matter, which facilitated the mobility of metal in soil by acting as a carrier through formation of soluble metal-organic complexes (McCarthy, Zachara 1989; Mahdavi, Jafari 2010). As organic matter decomposes, more soluble organic compounds are released (Merritt, Erich 2003). Increase or decrease in Ni availability with organic matter depended upon its soluble (fulvic acid) or insoluble constituents like humic acid (McBride 1995). According to Stevenson and Cole (1999), humic and fulvic acids form both soluble and insoluble complexes with Ni. Due to their lower molecular weights and higher contents of acidic functional groups, Ni complexes of fulvic acids are more soluble than those of humic acids. Nickel extracted with DTPA was generally larger with increasing addition of exogenous humic acid solutions than that without humic acid application, which was attributed to the formation of Ni–humic complexes that ensured a temporary bioavailability of Ni and prevented their rapid transformation into insoluble species (Halim *et al.* 2003).

The decrease in soil pH from 7.80 to 7.60 with the addition of FYM at day 90 might be associated with organic matter (OM) decomposition responsible for increased concentration of Ni in soil as was also found by Heckman *et al.* (1987), Campbell and Beckett (1988). Similarly, Usman *et al.* (2004) also attributed the increase in concentration of Ni in incubated sludge-amended soil to the formation of soluble Ni-organic ligands associations and to a resultant decrease in soil pH (from 8.14 to 7.54) but the soil used was sandy with low organic carbon and not artificially metal incubated. The fast decomposition rate of organic matter could consume oxygen, thus possibly affect the redox conditions of soils, one of the main factors for increasing Ni solubility along with a change in soil pH and CO_2 concentration (Ross 1994).

2.3. Availability of zinc

Availability of Zn showed a similar pattern as was observed in the case of Ni. In the absence of added organic matter, Zn in the control soil was 3.7 mg kg^{-1} at day 30 and only 50% of applied Zn (1.78 mg kg^{-1}) was recovered at the end of the experiment (Fig. 3). The FYM application decreased extractability of the native Zn from 3.5 mg kg^{-1} to 2.4 mg kg^{-1}. In Zn spiked soil without FYM, Zn decreased at all the sampling times, whereas in manure amended soil, the availability of Zn gradually increased until the end of the experiment from 163 at day 30 to 230 mg kg^{-1} at day 90 with 400 mg kg^{-1} of Zn application, respectively.

The AB-DTPA extractable Zn in response to FYM added soil increased with time (Fig. 3). Previously Almas *et al.* (2000) observed the parallel behavior of Zn but under a different environment as they used acidic clay loam and marine loam soil texture for their experiment; they reported that the addition of organic matter (pig manure) increased the solubility of Zn through the formation of soluble organo-metallic complexes. Catlett *et al.* (2002) concluded that binding of Zn^{2+} with OM has a significant positive impact on its solubility in fine silty neutral to alkaline calcareous soils. The decomposition of organic matter resulted in the production of low molecular organic acid like acetic, formic, oxalic, lactic, propionic, malic,
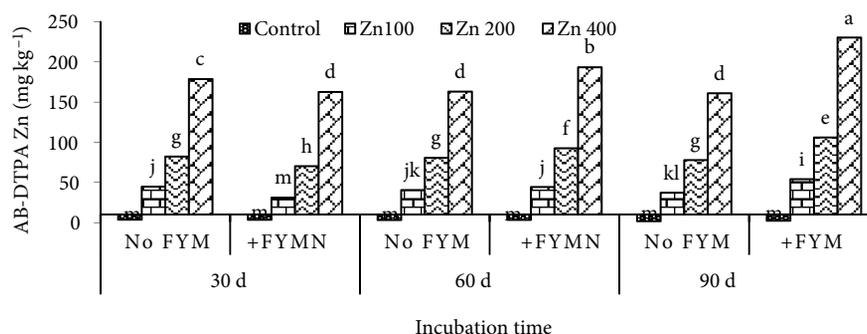

Fig. 3. Effect of incubation time on availability of Zn. FYM – farmyard manure; d – day. Lower case letters indicate the significance of treatments at P < 0.05

citric, and aconitic acids (Baziramakenga, Simrad 1998) to affect the pH perturbations as happened in our case the soil pH decreased 7.90 to 7.50 with the addition of organic matter at day 90 resulting increase in Zn availability.

At the end of our experiment, soluble organic components might have persisted resulting in higher availability of Zn. In addition, $CaCO_3$ in calcareous soils can lead to Zn precipitation as $ZnCO_3$ (Usman *et al.* 2004), but $ZnCO_3$ is soluble, hence more available. According to Lindsay (1979), minerals like ZnO (zincite) and $ZnCO_3$ (smithsonite) are too soluble to persist in soils. Antoniadis and Alloway (2002) reported increased extractability of Zn with an increase in dissolved organic carbon in sludge amended soils. In another study, Ashworth and Alloway (2004) found that Zn did not leach from columns filled with sewage sludge-amended sandy loam soil indicating its retention by soil. Pascual *et al.* (2004) reported lower Ni and Zn concentrations in unamended soil at the end of an incubation period of 64 days than those in the present study.

2.4. Availability of lead

Behavior of applied Pb was different from that exhibited by Ni and Zn (Fig. 4). With an incubation of FYM, the Pb availability decreased in metal–contaminated soil. In the unamended control, native Pb remained unchanged and its concentration was almost the same after 30, 60, and 90 days of incubation. The availability of Pb from the soil contaminated with 100, 200, and 400 mg kg^{-1} of Pb was 52, 98, and 224 mg kg^{-1}, respectively, after 30 days of incubation in the treatments with no FYM, which decreased by 40, 86, and 172 mg kg^{-1}, respectively, after 90 days of incubation. While the availability of Pb from the soil contaminated with Pb 100, 200 and 400 mg kg^{-1} on day 30 was 49, 104, and 214 mg kg^{-1} of the added Pb in the treatments with FYM, respectively. With FYM amended soil, available Pb was less than that in unamended soil and was 27, 79, and 161 mg kg^{-1} of the applied Pb at the end of the experiment, respectively. At the 100 mg kg^{-1} application rate, a decrease in availability was more than that at higher levels of Pb application.

In the present experiment, organic matter has an immobilization effect on Pb in soil. The AB-DTPA extractable Pb decreased at all levels of Pb addition but the decrease was more at the lowest rate of 100 mg Pb kg^{-1} of soil (Fig. 3). Similar findings where Clemente *et al.* (2006) reported EDTA-extractable Pb decreased from 42.7% of the total Pb in control samples to 37.3% in compost-treated samples and to 32.3% in manure treated samples. However, the experiment was conducted with different environment as they used sandy loam soil and followed McGrath and Cegarra (1992) procedure for metal extraction. Precipitation of Pb with $CaCO_3$ may also be responsible for the decreased availability of Pb (McBride 1994; Kumpiene *et al.* 2008). Over a 90-day incubation period, mobile Pb decreased to 0.62% of the total Pb contents in soil treated with compost (Usman *et al.* 2004). Precipitation of Pb, Zn, Cd, and Cu as insoluble compounds appeared to become important at approximately pH 6–7. At pH values of around 6 or 7, very little Pb is likely to be found in solution (Ram, Verloo 1985). This was attributed to the products like humic and fulvic acids resulting from decomposition of organic matter with which Pb formed stable organo-metallic complexes alone and in association with soil clays. As pointed out by Stevenson and Cole (1999), both fulvic and humic acids form soluble as well as insoluble complexes depending upon the degree of saturation. The importance of organic matter in limiting Pb availability has also been demonstrated by Strawn and Sparks (2000) and Saini and Gupta (2001).

Conclusions

From a soil and groundwater contamination point of view the retention of heavy metal in soil and their availability to plants is important. A calcareous loam soil was tested to investigate the effect of FYM on the availability of applied Ni, Zn, and Pb over a period of time. The availability of Ni and Zn increased with incubation time, but Pb availability decreased over time. Ostensibly, added FYM formed soluble organo-metallic complexes with Ni, and Zn increasing their availability with time. Whereas a decrease
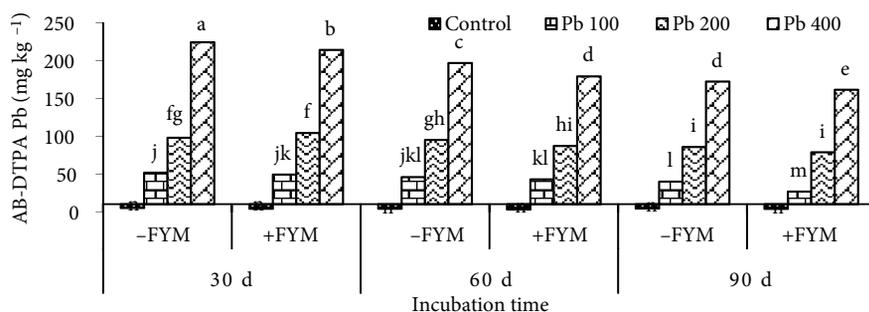

Fig. 4. Effect of incubation time on availability of Pb. FYM – farmyard manure; d – day. Lower case letters indicate the significance of treatments at P < 0.05

in Pb availability might be due to the presence of $CaCO_3$ resulting in its precipitation. The general order of affinity of heavy metal retention is as follows $Cu > Zn > Pb$.

Increased availability of Ni, and Zn with the application of farmyard manure could result in an increased risk to soil and groundwater resources. Continuous application of FYM with the passage of time not only significantly reduced metal sorption, but also increased their mobility through the formation of soluble metal complexes in alkaline soils and contaminates the groundwater through leaching of metals from these soils. During the application of FYM the nature, composition, physico-chemical properties of soil and microbial activities should be considered. More studies are needed to understand the phenomena of the increased availability of heavy metal by the addition of FYM and to prevent plants from their phytotoxic effect. However, the increased bioavailability of heavy metals by the application of farmyard manure can be used while phytoremediating the contaminated sites.

Disclosure statement

Authors declare no conflict of interest among them.

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