Soil Environ. 31(1): 55-66, 2012
www.se.org.pk
Online ISSN: 2075-1141
Print ISSN: 2074-9546

Effect of amendments on chemical immobilization of heavy metals in sugar mill contaminated soils

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Abstract

A bulk soil sample collected from the vicinity of PSM (Premier Sugar Mill) Mardan was amended with diammonium phosphate (DAP), triple super phosphate (TSP), Farm Yard Manure (FYM) and poultry manure (PM) in 1.5 kg soil in a 2 L plastic pot. Both DAP and TSP were added at 230 mg kg^{-1} (460 kg ha^{-1}) soil whereas the organic amendments (FYM and PM) were added at the rate of 10% by weight of soil. The air dried samples in pots were brought to field moisture content (0.33 bar water content) by the addition of either HIE (Hayatabad Industrial Estate) or PSM in two separate sets of experiments. The experimental pots were arranged in randomized complete design with three replicates under laboratory conditions during March to May (Temperature varying between 25 to 30 °C). Treated and control pots were incubated for 90 days al 0.33 bar ca 25% moisture and the moisture deficit during the incubation time was adjusted by adding PSM and HIE effluents in their respective set of experimental pots. Soil samples were collected after 15, 30, 45 and 90 d to determine the effect of amendments on AB-DTPA extractable metals. The results showed that AB-DTPA extractable Cd, Or, Cu, Ni and Cd increased significantly with lime and the maximum values were noted after 90 days incubation whereas the Fe, Mn and Zn content in soil increased with time but the increase was not significant. It was further noted that the increase over time in metal was not pronounced when supplied with amendments indicating their ability to chemically stabilize it compared to unamended soils. Higher values of all the heavy metals were noted in unamended soil. By comparing the different amendments, it was observed that FYM was effective in reducing the extractability/phytoavailability of all the metals under study except Pb whereby DAP was most effective as a stabilizing agent in the soil. It was concluded that in calcareous soil, FYM and DAP can be used to reduce the risk of phytotoxicity of heavy metals in contaminated soil or using wastewater for irrigation.

Keywords: Phytostabalization, amendments, industrial effluents, heavy metals, contaminated soil, incubation

Introduction

Pre-treatment of wastewater is always recommended before agricultural application but due to the high costs involved, in most places around the globe and more specifically in the developing countries, wastewater, irrespective of its origin is applied to the crops untreated. This application inflicts much of the unseen hazards into the food chain to which the farmers are oblivious, e.g. pathogenic infections, heavy metal accumulation and other toxic elements in the agricultural produce. Therefore, ways need to be found out to decrease the mobility of toxic heavy metals, rendering them less mobile and more stable, thereby decreasing their availability to the plant. One such method is the in situ chemical immobilization of heavy metals.

Chemical immobilization is the remediation technique of contaminant in soil that decreases the concentration of dissolved contaminants by sorption and or precipitation (Basta and McGowen, 2004). Increasing adsorption of metals or decreasing its solubility can reduce the risk of plant uptake, pollutant transport and its redistribution from contaminated sites. Immobilization of metals can be accomplished by the addition of amendments to reduce contaminant solubility or bioavailability to the plants. The addition of soil amendments, such as organic matter, phosphates, alkalizing agents, and biosolid can decrease solubility of metals in soil and minimize leaching to groundwater.

Fertilizer and waste products are used to chemically immobilize the heavy metals. Addition of phosphate materials has been proven useful as chemically immobilizing treatments. Ruby *et al*. (1994) indicated that adequate level of phosphate were responsible for the formation of insoluble complexes and the reduction in potentially bioavailable Pb. Khan and Jones (2009) reported that addition of lime resulted in significant reduction in the metal extractability with DTJPA and phytoavailability of

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Cu, Fe, and Zn while DAP was effective in lowering Pb extractability and phytoavailability. In their study, it was also reported that metal extractability decreased over time after applying different amendments including both organic and inorganic in acidic copper mine tailing soils. Research on chemical immobilization of heavy metals has included alkaline and phosphate based material that includes rock phosphate (apatite) and soluble phosphate (K.2lTP,i) but problems related to rate of release of phosphate have been encountered (too slow or loo fast, respectively) (Ma *et al.*, 1993; Laperche *et al.*, 1996; Hooda and Alloway, 1996; Derome, 2000). Other research has shown that highly soluble phosphate sources (DAP) are most effective for immobilizing Cd, Pb and Zn in soil (McGowen *et al.*, 2001). Few studies have investigated the use of municipal biosolids (sewage sludge), composts, manure and peat (Brown *et al.*, 1996: Basla and Sloan, 1999; Li *et al.*, 2000). Addition of organic materials buffers soil pH and reduces heavy metal uptake by plants. Organic matter with the reactive group such as hydroxyl, phenoxyl and carboxyl effectively controlled the adsorption and complexation of heavy metal and the activity of metals in the soil (Alloway, 1995; McBride *et al.*, 1997; Lee *et al.*, 2004 and Mahmood 2010).

Soil amendments are the major requirement for the successful establishment of vegetation in the metal-contaminated soils. The addition of amendment such as fly ash, sewage sludge, pig manure, is effective in lowering the metal toxicity of the soil and provides slow release of nutrient sources such as N, P. K to support plant growth (Wong, 2003; Chin *et al*., 2006). Cow manure, poultry manure and pig manure were found to be effective in reducing lead availability to plants, leading to lower uptake of lead (Scialdone *et al*., 1980; Wong and Lau, 1985). In addition, fertilizers are an essential ingredient for successful restoration of mine wastes (Bradshaw and Chadwick. 1980). Transmission of Cd, Pb, and Zn through the food chain is affected by the soil-plant barrier (Chancy and Giordano, 1977). The barrier limits transmission of metals through the food chain either by soil chemical processes that limit the solubility or by the plant senescence from phytotoxicity. Phosphate amendments that can immobilize Pb in contaminated soils include hydroxyapatite (Boisson *et al.*, 1999; Laperche *et al.*, 1997; Ma *et al.*, 1995: Khan and Jones, 2008, 2009).

Pakistan has a population of over 160 million and is one of the few countries that are almost completely dependent on a single river system for all its agricultural water demands. The Indus river and ils tributaries provide water lo over 16 million hectares of land, situated in the mainly arid and semi-arid zones of the country. A rapidly growing population, saline groundwater, a poorly performing irrigation distribution system, and recurrent droughts have led to increased water shortages. Under these conditions, the use of untreated urban wastewater for agriculture has become a common and widespread practice. These experiments aim at investigating the wastewater use looking at environmental and health risks together with the nutritive value of wastewater. The increasing use of wastewater and rapid industrialization generating wastewater requires research to minimize the risk associated with using such water and soils receiving it. In addition to this, the effectiveness of different chemical and organic amendments to immobilize heavy metals and decrease the potential entry of heavy metals into food chain, in an effort to find a safe and cheap way for using untreated wastewater for agricultural crops and also sec the long term effect of using wastewater on soil and crops.

Materials and Methods

Soil and amendments

A bulk sample of surface soil (<20 cm depth) receiving the effluents of Mardan Sugar Mill (SM) located in the vicinity of SM was collected to study the effect of different amendments on the phytoavailability of heavy metals. Soil was air dried and sieved (<2 mm) prior to further use in the experiment. The selected physical and chemical properties are summarized in Table 1. Particle size was determined using the hydrometer method (Gee and Bander, 1986). Moisture content was determined by oven drying (105 $^{\circ}$C, 24 h) whilst pH and electrical conductivity (EC) were determined in 1:1 (w/v) soil: water extracts (Smith and Doran, 1996). Calcium carbonate content was determined by acid neutralization method as given by Richard (1954) whereas organic matter content was determined by method given in Nelson and Sommer (1982).

Heavy metals in soil were determined by using AB-DTPA extractant according to the method given by Halvin and Soltanpour (1981) using atomic absorption spectrophotometer. The wastewater samples that were collected in bulk from sugar mill and Hayatabad Industrial Estate (HIE) are subsequently used for irrigating the incubating pots were filtered. The heavy metals from these samples were determined using atomic absorption spectrophotometer.

Four amendments *viz* diammonium phosphate (DAP), triple super phosphate (TSP), FYM and poultry manure (PM) were incorporated into soil (1.5 kg Soil in a 2 L plastic pot). The control consisted of 1.5 kg untreated soil. DAP and TSP were applied at 230 mg P kg^{-1} soil according to the earlier study of McGovven *el al.* (2001) who reported that 2300 mg P kg^{-1} as DAP was most effective in immobilizing Pb and Zn (the calculations were made based on the molar ratio of total P to total Zn and Pb whereby other metals understudy were not part of their study). The FYM and PM were added to the soil at 10% dry weight basis. This application rate is common when organic matter is used for restoration of contaminated soils (Sopper, 1993).

Table 1: Physico-chemical properties of soil

Property	Unit	Value
Sand	%	26.33
Silt	%	65.2
Clay	%	8.4
Textural Class		Silt loam
Organic matter	%	1.08
Lime Content	%	9.04
pH	-	8.3
EC	dS m^{-1}	0.32
SAR	(mmole $L^{-1})^{1/2}$	5.3
Cd	mg kg^{-1}	0.19
Cr	mg kg^{-1}	0.18
Cu	mg kg^{-1}	6.24
Fe	mg kg^{-1}	12.47
Mn	mg kg^{-1}	1.42
Ni	mg kg^{-1}	1.24
Pb	mg kg^{-1}	0.74
Zn	mg kg^{-1}	2.23

The experiment was split in two parts, i.e. one set was irrigated with the effluents collected from sugar mill and the other set of experiment was irrigated with HIE waste water (the irrigation was done to bring the incubating pots to field capacity (0.33 bar ca. 25% water). All the soil amendment treatments were performed in triplicate. The pots were kept in the laboratory (temperature varying from 25 to 30 °C, under laboratory conditions during March to May) for 90 days. Soil moisture was maintained (by adding the effluents of both locations) and the soils were mixed thoroughly at weekly intervals. Every 15 d after set up and until 90 d, soil samples (30 g) were collected from each treatment pot for metal analysis. Metal extraction was accomplished with AB-DTPA (Havlin and Soltanpour, 1981)

Statistical Analysis

All the data were subjected to two ways ANOVA using Genstat Discovery Edition 3, package for window (Rothamsted Research UK, 3rd Ed.). Means comparisons were made using LSD test after it was determined that *F-value* was significant at 5% level of probability.

Results and Discussion

Physico-chemical characteristics of soil and wastewater

The results of the physico-chemical properties of bulk soil collected from the site irrigated with effluents from Premier Sugar Mill (PSM) Mardan along with sugar mill wastewater (SM WW) and Hayatabad Industrial wastewater effluents (HIE WW) are given in Table 1 and 2. The soil was silt loam with alkaline pH (8.3). The electrical conductivity was low (0.32 dS m^{-1}) with organic matter content of 1.08%. The soil was moderately calcareous having 9.04% calcium carbonate. All the essential micronutrients (Cu, Fe, Mn and Zn) were well above the adequate levels of crops according to the AB-DTAP extractable soil test (Havlin and Soltanpour, 1981) whereas other metals (Cr, Cd, Ni and Pb) were within the permissible limits in soil (Kabata-Pendias and Pendias, 1995; EPA 1998). According to the NHQ standards for liquid industrial effluents and municipal wastes (EPA. 1998), the level of Cr, Cd, Cu, Fe, Ni and Pb were above the permissible limits in HIE effluents and only Cd, Pb and Ni were above the permissible limits in SM WW.

Table 2: Chemical properties of waste water (metal content is in mg L^{-1})

Property	HIE WW*	PSM WW**
pH	7.03	7.68
EC (d Sm^{-1})	4.09	1.03
SAR (mmole $L^{-1})^{1/2}$	0.33	3.24
Cd	0.23	1.78
Cr	5.68	0.13
Cu	1.29	0.68
Fe	21.94	60.71
Mn	1.34	0.07
Ni	0.21	1.34
Pb	3.06	0.63
Zn	0.53	0.29

*Hayatabad Industrial Estate Waste Water
** Premier Sugar Mill Waste Water

Results of AB-DTPA extractable Cd as affected by different treatments and incubation intervals (Table 3) showed that there were significant variations in Cd content of soil. There was a progressive increase in extractable Cd with time and the increase was more pronounced in PSM treated soil whereas the treatment effect was also significant compared to control soil. Significantly ($p < 0.05$) higher concentration of Cd with time was noted in control soil (in case of PSM) but this was not true in case of soil treated with HIE effluents. These variations mainly stem due to variations in the Cd level present in both the effluents. The addition of FYM was more effective in reducing Cd extractability compared to other treatments. Bolan *et al.* (2003) reported that addition of biosolid compost reduced the phytoavailability of Cd whereas Zwonitzer et al. (2003) and Bolan and Duraisamy (2003) reported the superiority of lime and P sources on reducing the phytoavailability of Cd in metal contaminated soils. The reason of lime superiority in their study was mainly due to the lower pH of soil used in their study while in the present study; the pH was higher with moderately calcareous nature of soil. By comparing the two sources of wastewater supplies (added to maintain the soil al field capacity on weekly basis), it was noted that comparatively higher values of Cd were noted in PSM (Figure 1 and 2). The reason of elevated level of Cd in PSM treated effluents may be the initially high level of Cd (1.78 mg kg^{-1}) compared to HIE treated effluents (0.23 mg kg^{-1}), Table 2.

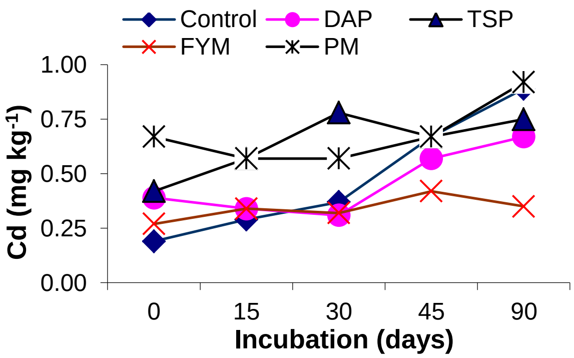

Figure 1: Effect of organic and inorganic treatments on Cd immobilization irrigated with HIE effluents

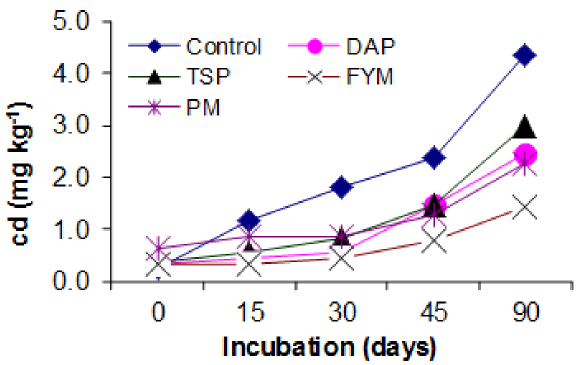

Figure 2: Effect of organic and inorganic treatments on Cd immobilization irrigated with PSM effluents

The results of the Cr concentration as affected by incubation interval, addition of amendments and irrigation with effluents sources (Table 4) were significant al 5% level of probability. The concentration of Cr increased with time and the magnitude of increase was different when amended with different organic and inorganic amendments. Significantly higher concentration of Cr was noted in the control soil and the lowest was noted in soil treated with FYM. The variation among the amendments were non-significant. By-comparing the two sources of effluents (Figure 3 and 4), it was noted that higher values were recorded in soil irrigated with HIE and lower in the PSM that was mainly due to the initially higher concentration present in HIE effluents. Bolan and Duraisamy (2003) reported the effectiveness of organic amendments in reducing the extractability and phytoavailability of Cr in contaminated soils.

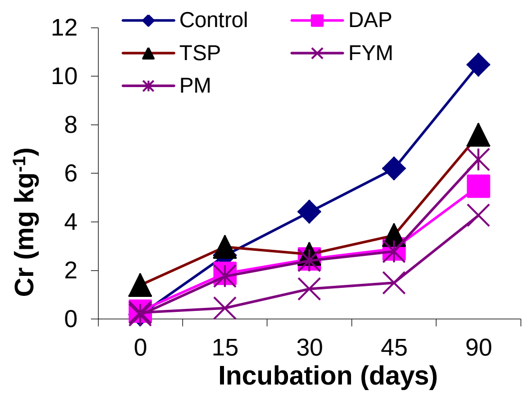

Figure 3: Effect of amendments on Cr immobilization in soil with time irrigated with HIE effluents

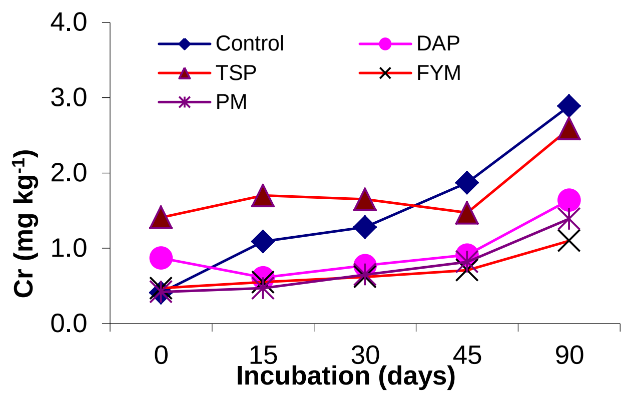

Figure 4: Effect of organic and inorganic amendments on Cr immobilization in soil irrigated with PSM effluents

The addition of amendments reduced the Cu contents extracted with AB-DTPA extraction, but the reduction was not significant ($p < 0.05$) compared to control (Table 5). Although non-significant, FYM was effective in stabilizing Cu in soil. The extractability of Cu with time increased linearly although the increase was non-significant. The net release over time (Table 5) was comparable regardless of the amendment additions. By comparing the sources of effluents, comparatively higher values were noted when irrigated with PSM compared to HIE (Figure 5 and 6) although the initial level of Cu was higher in HIE but did not offset the concentration of Cu in soil as the extractability of Cu is driven by soil pH, lime and organic matter content of the media. Khan and Jones (2009) reported that Cu extractability was reduced over time in soil treated with green compost and lime whereas DAP enhanced the phytoavailability of Cu and the reason of the enhanced availability in their study due to DAP may be because of the very high level of DAP application (2300 mg) and low soil pH (3.29).

The effect of the amendments on the AB-DTPA extractable Fe was more pronounced in soil irrigated with PSM compared to HIE irrigated soil and the order of Fe reduction due to amendment was FYM > PM > TSP > DAP and control (Table 6 with respect to net release over 90 days incubation interval). By comparing the two sources of effluent irrigation (Figure 7 and 8), it was noted that in HIE irrigated soil, the trend of Fe extraction with time was not consistent and the changes over time in Fe concentration were not significant. The soil amended with PSM (as an irrigation) showed a linear increase in Fe content with time and the variations were significant. The reason of higher values in SM added effluents may be due to the initially higher concentration of Fe compared to HIE. The addition of both the organic amendments (FYM and PM) significantly reduced Fe content in soil with respect to the overall net release over time. The overall results showed that the Fe content in soil was above the critical level of crop requirements (Havlin and Soltanpour, 1981) but not an excessive range lo be toxic. The results are in agreement to the previous work of Hooda and Alloway, (1996), Hettiarachchi and Pierzynski (2002) and Khan and Jones (2008, 2009).

Table 3: Effect of amendments and incubation interval (days) on extractable Cd content (mg kg^{-1}) of soil irrigated with HIE and PSM wastewater

Cd	Source of WW	0	15	30	45	90	Net release
Control	HIE	0.19	0.29	0.37	0.67	0.89	0.70*
DAP		0.39	0.34	0.31	0.57	0.67	0.28
TSP		0.42	0.57	0.78	0.67	0.75	0.33
FYM		0.27	0.34	0.32	0.42	0.35	0.08
PM		0.67	0.57	0.57	0.67	0.92	0.25
Control	PSM	0.23	1.16	1.80	2.38	4.35	4.12
DAP		0.34	0.45	0.57	1.47	2.47	2.13
TSP		0.38	0.55	0.81	1.47	2.97	2.59
FYM		0.31	0.32	0.45	0.78	1.42	1.11
PM		0.61	0.87	0.84	1.29	2.27	1.66

**Net release is the difference between metal content on day 0 and after 90 days of incubation. Note the amendments were added 10 days before keeping the samples for incubation and were mixed thoroughly.*
$LSD_{(0.05)}$ for Treatment and Incubation internal mean = 0.14; $LSD_{(0.05)}$ for Effluent mean (combine mean) = 0.09

Table 4: Effect of amendments and incubation interval (days) on extractable Cr content (mg kg^{-1}) of soil irrigated with HIE and PSM wastewater

Cr	Source of WW	0	15	30	45	90	Net release
Control	HIE	0.18	2.62	4.41	6.19	10.47	10.29
DAP	HIE	0.33	1.88	2.47	2.89	5.47	5.14
TSP	HIE	1.40	2.97	2.67	3.45	7.58	6.18
FYM	HIE	0.26	0.45	1.24	1.49	4.27	4.01
PM	HIE	0.17	1.76	2.41	2.78	6.57	6.40
Control	PSM	0.41	1.09	1.28	1.87	2.89	2.48
DAP	PSM	0.87	0.61	0.77	0.91	1.64	0.77
TSP	PSM	1.41	1.70	1.65	1.47	2.59	1.18
FYM	PSM	0.47	0.55	0.62	0.71	1.10	0.63
PM	PSM	0.42	0.47	0.65	0.82	1.39	0.97

$LSD_{(0.05)}$ Treatment mean = 0.23; $LSD_{(0.05)}$ for Effluents mean = 0.19; $LSD_{(0.05)}$ for incubation interval = 0.23
Results are statistically non significant

Table 5: Effect of amendments and incubation interval (days) on extractable Cu content (mg kg^{-1}) of soil irrigated with HIE and PSM wastewater

Cu	Source of WW	0	15	30	45	90	Net release
Control	HIE	6.24	6.82	7.23	7.83	8.93	2.69
DAP	HIE	6.27	6.42	6.60	6.71	6.72	0.45
TSP	HIE	6.25	6.65	6.95	7.33	7.24	0.99
FYM	HIE	6.17	6.17	6.08	6.05	6.24	0.07
PM	HIE	6.31	6.68	6.85	6.87	7.34	1.03
Control	PSM	6.25	7.09	7.70	8.46	9.71	3.46
DAP	PSM	6.34	6.52	6.42	6.85	7.14	0.80
TSP	PSM	6.28	6.75	6.78	7.21	7.34	1.06
FYM	PSM	6.41	6.45	6.62	6.46	6.75	0.34
PM	PSM	6.36	6.66	6.97	7.35	7.43	1.07

Results are statistically non-significant

Table 6: Effect of amendments and incubation interval (days) on extractable Fe content (mg kg^{-1}) of soil irrigated with HIE and PSM wastewater

Fe	Source of WW	0	15	30	45	90	Net release
Control	HIE	12.47	13.43	14.10	14.77	16.92	4.44
DAP	HIE	12.64	12.59	13.28	14.98	14.87	2.23
TSP	HIE	12.69	11.56	14.33	14.98	14.58	1.89
FYM	HIE	14.72	11.24	12.33	13.47	12.57	-2.15
PMR	HIE	13.47	13.47	14.20	14.14	13.24	-0.23
Control	PSM	11.97	28.95	40.43	45.47	76.45	64.48
DAP	PSM	12.64	21.14	22.14	27.58	28.47	15.83
TSP	PSM	12.46	15.47	21.47	34.52	33.47	21.01
FYM	PSM	14.17	16.47	16.89	21.14	21.89	7.72
PM	PSM	13.87	14.57	18.47	19.58	26.89	13.02

$LSD_{(0.05)}$ for treatments mean = 1.66; $LSD_{(0.05)}$ for Effluents mean = 0.83
$LSD_{(0.05)}$ for Incubation interval = 1.66

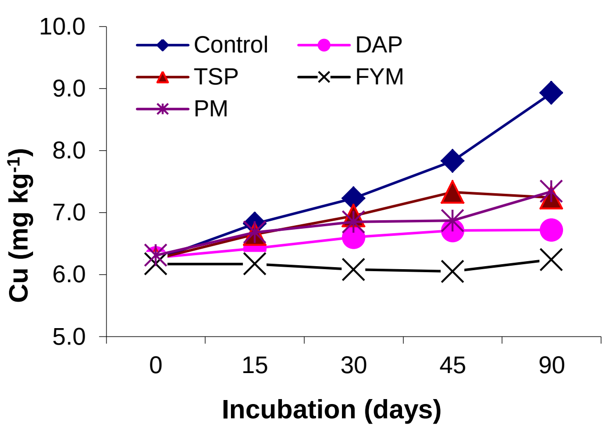

Figure 5: Effect of organic and inorganic treatments on Cu immobilization in soil irrigated with HIE effluents

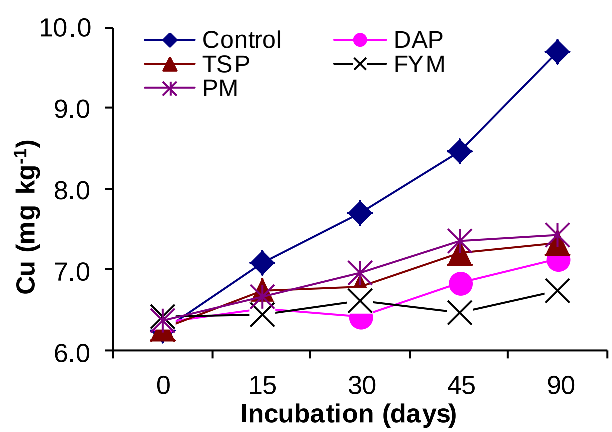

Figure 6: Effect of organic and inorganic treatments on Cu immobilization in soil irrigated with PSM effluents

Table 7: Effect of amendments and incubation interval (days) on extractable Mn content (mg kg^{-1}) of soil irrigated with HIE and PSM wastewater

Mn	Source of WW	0	15	30	45	90	Net release
Control	HIE	1.42	2.13	2.84	3.23	5.56	4.14
DAP	HIE	1.65	1.85	2.14	2.30	3.18	1.53
TSP	HIE	1.53	1.82	2.55	2.84	3.68	2.15
FYM	HIE	1.48	1.75	1.95	2.17	2.34	0.86
PM	HIE	1.62	1.70	2.08	2.38	2.91	1.29
Control	PSM	1.30	1.49	1.85	2.15	2.69	1.39
DAP	PSM	1.65	1.83	1.74	1.74	1.84	0.19
TSP	PSM	1.48	1.67	1.78	1.89	2.24	0.76
FYM	PSM	1.64	1.70	1.65	1.74	1.74	0.10
PM	PSM	1.72	1.64	1.84	2.01	1.95	0.23

$LSD_{(0.05)}$ for treatments mean = non significant; $LSD_{(0.05)}$ for Effluents mean = 0.07; $LSD_{(0.05)}$ for Incubation interval = 0.24

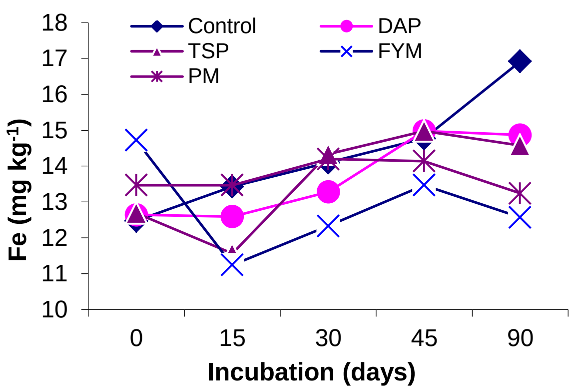

Fig. 7: Effect of amendments on Fe immobilization in soil irrigated with HIE effluents

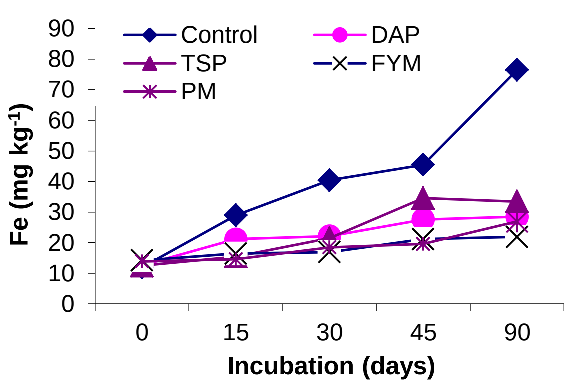

Figure 8: Effect of amendments on the immobilization of Fe in soil irrigated with PSM effluents

The effect of organic and inorganic treatments and sources of effluents on Mn content in soil were short of significance ($p < 0.05$) and so was their interaction whereas the Mn content was significantly enhanced with incubation interval (Table 7). Significantly higher values were noted in control soil while the trend of Mn content up to the first two weeks remained fairly constant and then changed slightly indicating the stabilizing effect of Mn due to amendments. Although non-significant, FYM proved better in reducing the extractability of Mn in soil. Francisco *et al.* (2006) reported that the addition of urban waste compost to the barley reduced Mn concentration in the dry matter indicating its stability in soil. By comparing the two sources of wastewater, it was noted that higher values were recorded in HIE compared to PSM (Figure 9 and 10).

The AB-DTPA extractable Ni followed the same trend as was noted for other metals i.e. Ni content increased with incubation intervals and the increase was significantly higher in control (Table 8). The variation between different treatments were also significant and FYM proved better in reducing the extractability with time in both the HIE and SM irrigated soils (Figure 11 and 12). The effect of DAP, FYM and poultry manure on stabilizing Ni in soil remained the same being non-significant among themselves but significantly lower Ni was extracted compared lo control. Sabir *et al*. (2008) reported that FYM and activated carbon were effective in reducing AB-DTPA extractable Ni from soil after 30 days of incubation compared to poultry manure and press mud. The significant reduction in Ni extractability / phytoavailability with FYM may be formation of insoluble Ni and organic matter complexes (Halim *et al*., 2003; Karaca, 2004).

Lead (Pb) is one of the most widely studied metals as a pollutant in the agriculturally contaminated soils. The effect of amendments, incubation interval and effluents applied had a significant ($p < 0.05$) effect on the AD-DTPA extractable Pb and so were their interactions (Table 9). Unlike all other metals studied, it was noted that DAP was most effective in stabilizing Pb in soil over time. The net release in both effluent treated soils was minimum when DAP was applied whereas the maximum net release over time was noted in control soil (Table 9).

The response *of* Pb to application of TSP was similar as DAP in PSM irrigated soil but was not true in case of HIE soil and that may be due to the initially higher values of Pb in HIE effluents (Figure 13 and 14). These results are

Table 8: Effect of amendments and incubation interval (days) on extractable Ni content (mg kg^{-1}) of soil irrigated with HIE and PSM wastewater

Ni	Source of WW	0	15	30	45	90	Net release
Control	HIE	1.24	2.66	3.65	4.64	7.81	6.57
DAP	HIE	1.52	1.74	2.14	2.50	3.27	1.75
TSP	HIE	1.45	1.55	2.55	3.45	4.14	2.69
FYM	HIE	1.35	1.34	1.85	1.85	2.18	0.83
PM	HIE	1.79	2.15	2.47	2.89	3.85	2.06
Control	PSM	1.31	2.46	3.01	3.53	5.27	3.96
DAP	PSM	1.55	2.14	2.04	2.63	2.89	1.34
TSP	PSM	1.34	2.18	2.51	2.75	3.75	2.41
FYM	PSM	1.42	1.85	1.75	1.87	2.10	0.68
PM	PSM	1.67	2.24	2.31	2.41	3.14	1.47

$LSD_{(0.05)}$ for treatments mean = 0.3;, $LSD_{(0.05)}$ for Effluents mean = non significant; $LSD_{(0.05)}$ for Incubation interval = 0.3

Table 9: Effect of amendments and incubation interval (days) on extractable Pb content (mg kg^{-1}) of soil irrigated with HIE and PSM wastewater

Pb	Source of WW	0	15	30	45	90	Net release
Control	HIE	0.74	2.77	4.20	5.62	10.17	9.43
DAP		0.95	1.54	2.15	2.98	3.47	2.52
TSP		1.24	2.05	3.17	4.15	7.34	6.10
FYM		1.10	1.31	2.75	3.47	4.68	3.58
PM		1.31	1.78	2.67	3.84	5.47	4.16
Control	PSM	0.83	1.69	2.27	3.14	4.61	3.78
DAP		1.24	1.32	2.16	2.24	2.74	1.50
TSP		1.41	1.47	2.24	2.84	3.14	1.73
FYM		1.33	1.54	1.67	2.67	2.64	1.31
PM		1.27	1.24	2.67	2.31	2.47	1.20

$LSD_{(0.05)}$ for treatments mean = 0.26; $LSD_{(0.05)}$ for Effluents mean = 0.13; $LSD_{(0.05)}$ for Incubation interval = 0.26

Table 10: Effect of amendments and incubation interval (days) on extractable Zn content (mg kg^{-1}) of soil irrigated with HIE and PSM wastewater

Zn	Source of WW	0	15	30	45	90	Net release
Control	HIE	2.23	2.54	2.75	2.96	3.65	1.42
DAP		2.35	2.42	2.65	2.74	2.78	0.43
TSP		2.45	2.50	2.65	2.85	3.24	0.79
FYM		2.24	2.42	2.45	2.34	2.47	0.23
PM		2.46	2.35	2.65	2.75	2.85	0.39
Control	PSM	2.36	2.89	3.25	3.58	4.70	2.34
DAP		2.31	2.51	2.55	2.84	2.57	0.26
TSP		2.41	2.66	2.85	2.97	3.23	0.82
FYM		2.15	2.65	2.68	2.57	2.61	0.46
PM		2.34	2.74	2.87	3.05	2.99	0.65

The results are statistically non-significant consistent with those reported in other studies (Chen *et al.*, 2003; Basta and McGowen, 2004; Khan and Jones, 2008, 2009). The efficiency of DAP on immobilization of Pb may be due to the formation of anglesite ($PbSO_4$) or lead phosphate that may control the Pb solubility in soil (McGowen *et al.*, 2001). Basta and McGowen (2004) reported that the formation of lead 254 hvdroxypyromorphite [$Pb(P0_4)3OH$] after application of DAP was the most probable solid phase controlling Pb solubility in many soils which supported the conclusion that DAP would be more effective treatment than lime or other organic amendments.

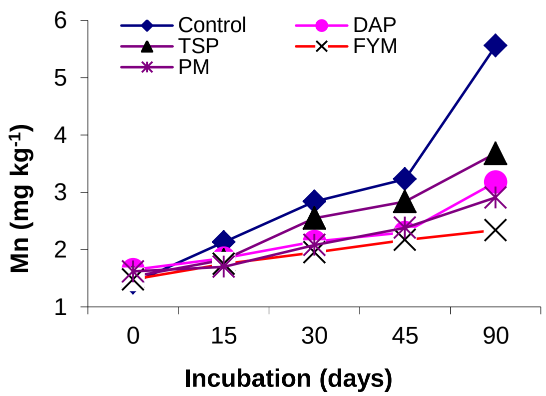

Figure 9: Effect of amendments on Mn immobilization in soil receiving HIE effluents

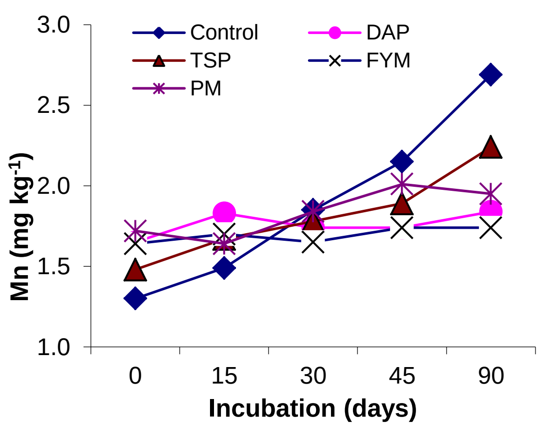

Figure 10: Effect of amendments on Mn immobilization in soil receiving PSM effluents

Results of the various organic and inorganic amendment treatments on Zn followed the same trend as was noted for all other metals under study but were slightly different than Pb (Table 10). The effect of amendments application was non-significant, however. FYM had an edge in immobilizing soil Zn over time compared to other treatments. The maximum net release over time was higher in the control soil. Similar results were reported by Sabir et al (2008). By comparing the two sources of wastewater application, it was noted that there were no significant variations (Figure 15 and 16).

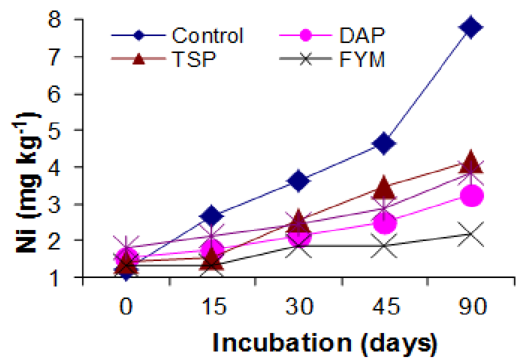

Figure 11: Effect of amendments on Ni immobilization in soil receiving HIE effluents

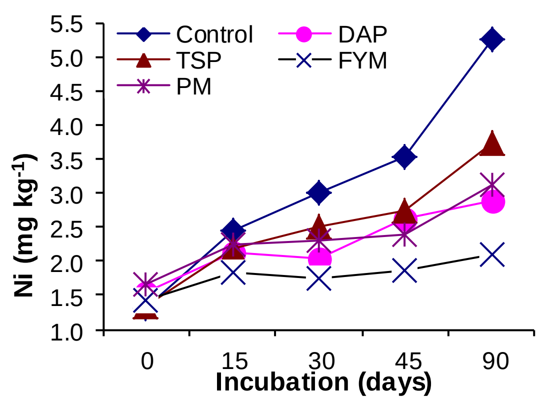

Figure 12: Effete of amendments on Ni immobilization in soil receiving PSM effluents

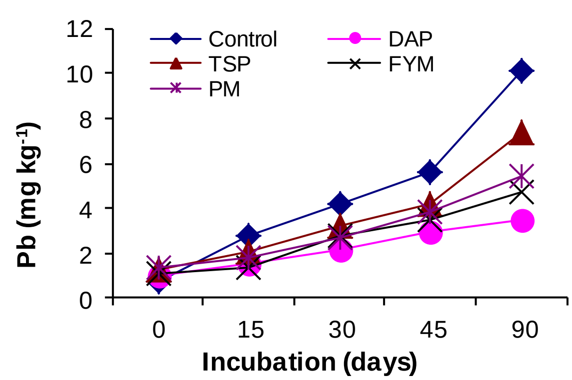

Figure 13: Effect of amendments on Pb immobilization in soil receiving HIE effluents

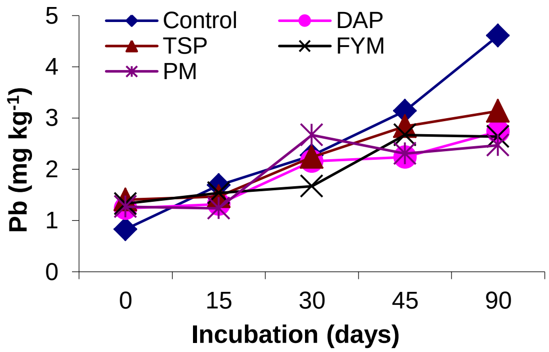

Figure 14: Effect of amendments on Pb immobilization in soil receiving PSM effluents

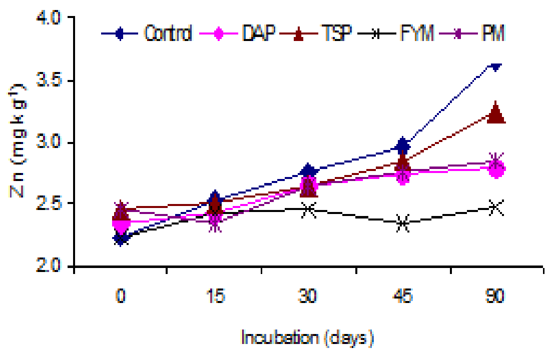

Figure 15: Effect of amendments on Zn immobilization in soil receiving HIE effluents

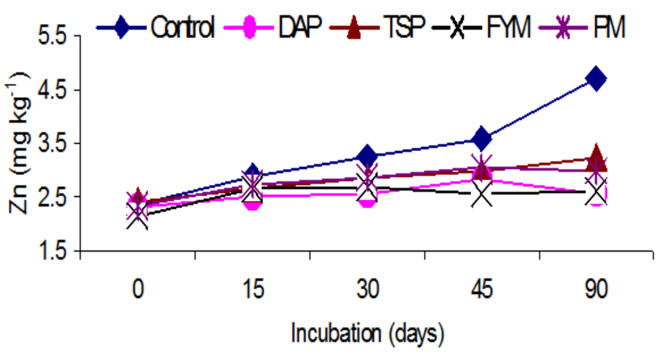

Figure 16: Effect of amendments on Zn immobilization in soil receiving PSM effluents

Conclusion

According to the NHQ standards for liquid industrial effluents and municipal wastes (NEQS 1998). the level of Cr, Cd, Cu. Ni and Pb were above the permissible limits in HIE effluents and Cd, Cu, Fe and Ni were above the permissible limits in PSM. The concentration of Cr, Cu, Ni and Pb in all industrial effluents was found above the USEPA (1999) standard for irrigation water thus these effluents are not suitable for irrigation purposes. The concentration of AB-DTPA extractable Cd. Cr. Cu, Ni and Cd increased with time and the maximum values were noted after 90 days incubation interval. The AB-DI'PA extractable Fe, Mn and Zn content in soil increased with time but the increase was not significant. Higher values of all the heavy metals were noted in unamended soil indicating its build up that may be subsequently released from the soil with time to crops grown on such soils. By comparing the different amendments, it was concluded that FYM was effective in reducing the phytoavailability by making insoluble chemical complexes of all '.he metals under study except Pb and Zn whereby DAP was most effective in chemically stabilizing it in the soil. It was further concluded that in calcareous soil, FYM can be used to reduce the phytotoxicity of heavy metals in contaminated soil or using wastewater for irrigation.

Acknowledgement

The authors are thankful to the Higher Education Commission, Pakistan for providing financial sport.

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