

Contents lists available at ScienceDirect

Journal of Geochemical Exploration

journal homepage: www.elsevier.com/locate/jgeoexp

In-situ stabilization of heavy metals in agriculture soils irrigated with untreated wastewater



CrossMark

Farmanullah Khan ^{a,b,*}, Mohammad Jamal Khan ^{a,c}, Abdus Samad ^a, Yousaf Noor ^d, Muhammad Rashid ^a, Bismillah Jan ^{a,b}

^a Department of Soil & Environmental Sciences, The University of Agriculture, Peshawar, Pakistan

^b Directorate of Soil and Water Conservation Khyber Pakhtunkhwa, Peshawar, Pakistan

^c Institute of Soil Science, Chinese Academy of Sciences, Nanjing, PR China

^d Agriculture Research Institute, Peshawar, Pakistan

ARTICLE INFO

Article history: Received 24 December 2014 Revised 17 May 2015 Accepted 5 July 2015 Available online 21 July 2015

Keywords: Heavy metal pollution Wastewater Soil amendments In-situ stabilization

ABSTRACT

A field experiment was conducted to assess the effectiveness of various organic and inorganic amendments on the in-situ stabilization of common heavy metals (Cd, Cr, Cu, Fe, Mn, Ni, Pb and Zn) added to soil through wastewater irrigation. Analysis of wastewater samples indicated higher concentrations of Cr, Cu, Fe, and Pb as compared to the safe limits set by the NEQS for effluents and wastewater, indicating a potential buildup of the metals in soil, whereas the concentrations of Cd, Ni, Mn and Zn were within the safe limits for use as irrigation water. The soil of the experimental plots (size: 1×2 m, design: RCBD) was loam with an alkaline pH of 8.1 and an EC of 0.32 dS m⁻¹ (1:5 soil water suspension). Organic matter content of the soil was 1.08% while lime content was 9.04%. The analysis of soils post-experiment indicated a varied effect of different amendment on the stability of different metals. The concentration of Ni and Pb buildup in wastewater irrigated plots was higher in comparison to control plot receiving tap water and may cause soil toxicity if untreated wastewater is used for long term. Farm yard manure (FYM) was effective in stabilizing Cr, Fe, Mn, Ni, and Pb in soil. Di-ammonium phosphate (DAP) was more effective in immobilizing Cd, Cu, and Zn in soil. The use of FYM at 10 t ha⁻¹ and DAP at 120 kg P ha⁻¹ reduced the metal mobility in soil probably by forming insoluble complexes with metals and are thus recommended as soil amendments where untreated wastewater is used in urban agriculture so as to limit the entry of heavy metals into the food chain.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

In Pakistan, about 26% of national vegetable crops is irrigated with wastewater (Ensink et al., 2004). With the growth in population and the increase in consumption of freshwater in domestic use, the use of wastewater is bound to increase in agriculture for the production of food crops (Scott et al., 2004). Around 70% of the water utilized in cities is refused as wastewater (Scott et al., 2004) and its volume has increased with increase in population and economic development (Qadir et al., 2008; Huibers et al., 2004).

In spite of the risks, direct application of urban wastewater to crops is a common and an ancient practice around urban centers (Huibers et al., 2004) especially in the big cities of Pakistan (Ullah et al., 2011). Although discouraged, because of the associated health hazards, the use of wastewater is increasing because of the scarcity of irrigation water resources and the growing volumes of urban wastewater

E-mail address: sescientist@hotmail.com (F. Khan).

generated in developing countries. Some researchers have estimated that more than 20 mha in 50 countries are currently irrigated with urban wastewater. A study by the International Water Management Institute (IWMI) has estimated that 32,500 ha of agriculture land in Pakistan is irrigated directly with untreated wastewater (Ensink et al., 2004).

The treatment of wastewater is a costly process and therefore, in many countries of the world, wastewater treatment systems are hardly functioning or have very low coverage, which has resulted in the use of very poor quality water for irrigation of agricultural crops. This unchecked application of wastewater can create significant risks to public health, particularly in expanding urban areas (Drechsel et al., 2010). The vegetables grown in soil irrigated with untreated domestic wastewater and sewage sludge showed high level of heavy metals when compared with control samples (Jamali et al., 2007).

The wastewater used for irrigation is a rich source of nutrients (Kennish, 1992) and rewards back in terms of increased agriculture and income, if the associated risks are neglected altogether. Ensink et al. (2004) have estimated income of farmers using wastewater to be around US\$ 300 more per annum than the ones using freshwater.

^{*} Corresponding author at: Directorate of Soil and Water Conservation, ATI Campus Opposite Islamia College, University Road, Peshawar, Pakistan.

When wastewater, however, is used for the growing of crops for a prolong period, the heavy metals present in it accumulate in soil overtime (Ghosh et al., 2012; Ullah et al., 2011; Khan et al., 2008) which, in turn, may be absorbed by the plants in concentrations considered to be phyto-toxic (Kirkham, 1983).

The wastewater generated in cities generally comes from domestic sewage, commercial establishments, industry and other urban runoff (Scott et al., 2004). Such wastewater is mostly contaminated with trace elements like lead (Pb), copper (Cu), lead (Pb), cadmium (Cd), zinc (Zn), boron (B), cobalt (Co) chromium (Cr), arsenic (As), molybde-num (Mo), and iron (Fe) (Kanwar and Sandha, 2000) apart from many harmful microbes and persistent organic pollutants (POP's). Therefore, ways need to be explored to decrease the mobility of toxic heavy metals in soil, rendering them less mobile and more stable. The stability of heavy metals in soil can restrict their entry into the plant body, and ultimately the food chain. One such method is the phyto-stabilization of heavy metals (Pierzynski et al., 2000).

Since the solubility of a contaminant is related to its immobility and bioavailability, chemical immobilization may prove better in reducing the associated environmental risks (Wong and Lau, 1985). Soil amendment is considered as a major source for stabilization of heavy metals in soil. The addition of amendment such as fly ash, sewage sludge and pig manure has been reported to be effective in lowering the metal toxicity of the soil and provide slow release of nutrient sources such as N, P, and K to support plant growth (Wong, 2003; Chiu et al., 2006). Xardalias et al. (2013) found in their study that Zeolite treatments decreased statistically significantly the availability of Ni, Cd, and Co to plants, decreased the heavy metal soil pollution level assessed by the Elemental Pollution Index (EPI), and Pollution Load Index (PLI), respectively, and the Radish root yield at the early harvest, but its effect on the later harvest was not statistically significant.

Intensive research work has been carried out on the effectiveness of an amendment on the stability of one or two heavy metal polluting a particular site for exploring safer and cost-effective ways to deal with heavy metals contamination. For instance, Bolan et al. (2003) reported that addition of bio-solid compost reduced the mobility of Cd in soil. DAP also showed a reduction in the mobility of Cd in soil confirming the results of Zwonitzer et al. (2002). Similarly, Khan and Jones (2009) reported that Cu extractability was reduced over time in soil treated with green compost and lime. Wong and Lau, 1985 concluded that organic manures such as farm yard manure, poultry manure, and pig manure were found to be effective in reducing lead availability to plants, leading to lower uptake of lead. Boisson et al., 1999; Laperche et al., 1997; Ma et al., 1995; Khan and Jones, 2008 have reported the superiority of phosphate amendments to immobilize Pb in contaminated soils.

The wastewater around cities carries within it a wide range of metal pollutants i.e. Cd, Cr, Cu, Fe, Mn, Ni Zn, Pb and therefore the present study was designed to investigate the effectiveness of different chemical (phosphoric fertilizers — di-ammonium phosphate and triple super phosphate) and organic amendments (humic acid, farm yard manure and poultry manure) on their ability to immobilize the most commonly reported heavy metals in urban wastewater and reduce their potential entry into food chain, in an effort to find a cost-effective and safer way for application of untreated wastewater to agricultural crops. The current research is an effort for exploring an instant solution to minimize heavy metal uptake by crops in the vicinity of urban centers around the world where untreated wastewater is used, until a practical and cheap technique for wastewater treatment is devised to undo the harms of heavy metal pollution.

2. Methods and materials

The experiment was conducted on the 1×2 m field plots laid out in Randomized Complete Block Design and replicated three times. Alfalfa was chosen as a case crop and cultivated through broadcast method in

Table 1

Nature ai	nd rate o	fameno	lments	app	licati	ion	to s	soil.
-----------	-----------	--------	--------	-----	--------	-----	------	-------

S. No.	Nature of treatment	Rate of application		
1.	Tap water + No amendment	No amendment		
2.	Wastewater + No amendment	No amendment		
3.	Wastewater + Humic acid (HA)	2.5 Kg ha ⁻¹		
4.	Wastewater + (DAP)	120 Kg P ha ⁻¹		
5.	Wastewater + Triple super phosphate (TSP)	120 Kg P ha ⁻¹		
6.	Wastewater + Farm yard manure (FYM)	10 t ha ⁻¹		
7.	Wastewater + Poultry manure (PM)	10 t ha ⁻¹		

standing water. The treatments applied are given in Table 1. The plots were irrigated with two sources of water: wastewater and tube-well water. Wastewater was collected from the Malakandhere wastewater channel that drains the effluents from Hayatabad Industrial Estate (HIE) Peshawar, Pakistan, in addition to sewage and rain water. The wastewater was applied to the crop as per crop requirement.

2.1. Soil analysis

A composite soil sample (0–30 cm depth) from experimental plot was collected, air dried, crushed, and passed through ≤ 2 mm sieve and analyzed for common heavy metals using AB-DTPA extraction according to the method given by Havlin and Soltanpour (1981). Particle size analysis was determined using hydrometer method (Gee and Bauder, 1986), while pH was determined in 1:5 (w/v) soil: water extract and electrical conductivity (EC) determined in 1:5 (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).

2.2. Wastewater analysis

Water samples were collected at different intervals from the wastewater drain and were analyzed for physico-chemical characteristics including pH, EC. The heavy metals were determined using Atomic Absorption Spectrophotometer.

2.3. Fresh biomass of alfalfa

Fresh biomass produced in each mini-plot was determined separately using an electronic balance immediately after each cut in the field to assess the increase in yield over control.

2.4. Statistical analysis

The data was analyzed using Statistix 8.1 and Genstat Discovery Edition 3 package (Steel and Torrie, 1980).

3. Results and discussion

The soil and water samples were analyzed for different physicochemical properties and metals including Cd, Cr, Cu, Fe, Mn, Ni, Pb, and Zn. The soil of the experimental site was silt loam with pH value slightly alkaline and moderately calcareous (CaCO₃ = 12.5%). The EC was 0.54 dS m⁻¹ with the organic matter content of 1.02% (total organic nitrogen less than 0.2 g kg⁻¹) that may not support productive agriculture without the temporal addition of various fertilizers.

3.1. Wastewater characteristics

The pH of wastewater samples, collected at different times from the industrial wastewater channel, had a mean value of 7.3 (\pm 0.08; Table 2), which is not likely to induce any problems. The pH of the tube well/tap water (7.66) was slightly higher than wastewater samples.

Table 2

Properties of wastewater and freshwater samples collected from the Malakandhere Wastewater drain and tube-well at different times.

Properties	Unit	Waste water	Tap water
pН	-	7.03 (±0.08)	7.66 (±0.13)
EC	dS m ⁻¹	$1.49(\pm 0.08)$	0.34 (±0.07)
Cd	$mg L^{-1}$	0.25 (±0.04)	Not detected
Cr	$mg L^{-1}$	0.21 (±0.03)	Not detected
Cu	$mg L^{-1}$	$1.12(\pm 0.04)$	$0.09(\pm 0.04)$
Fe	$mg L^{-1}$	20.47 (±0.31)	0.14 (±0.04)
Mn	$mg L^{-1}$	$0.84(\pm 0.29)$	$0.06(\pm 0.08)$
Ni	$mg L^{-1}$	$0.13(\pm 0.03)$	Not detected
Pb	$mg L^{-1}$	$3.34(\pm 0.09)$	0.05 (±0.18)
Zn	$mg L^{-1}$	0.66 (±0.16)	$0.07 (\pm 0.09)$

Values are a mean of samples taken at different intervals.

Values in parenthesis indicate standard deviation.

The EC of samples, collected from the industrial wastewater channel was 1.49 (\pm 0.08 dS m⁻¹). The EC values of wastewater are higher than normal and may induce salinity problems compared to tube-well water. The tube-well water is of good quality having negligible content of heavy metals (USEPA, 1999 standard for irrigation water). The concentration of Cd, Cr, Cu, Fe, Mn, Ni, Pb, and Zn in wastewater is presented in Table 2. According to the National Environmental Quality Standards (NEQS) for liquid industrial effluents and municipal wastes (USEPA, 1998–1999), the levels of Cr, Cu, Fe, and Pb were above the permissible limits in the wastewater samples. While as per the USEPA (1999) standards for irrigation water, two heavy metals: Cr and Cu, were above the permissible limits.

3.2. Soil analysis

A composite soil sample was taken from the plots before sowing of the crop to determine the physico-chemical characteristic of the soil (Table 3). Soil samples were also taken individually from each plot before sowing and following the conclusion of the field experiment was analyzed for the following parameters:

3.2.1. Physico chemical properties of soil

The soil of the experimental site was loam in texture with alkaline pH (8.3). The Electrical Conductivity (EC) was low (0.32 dS m^{-1}) with organic matter content of 1.08%. The soil was moderately calcareous having lime content of 9.04%. All the essential metals i.e. Cu, Fe, Mn, and Zn were well above the adequate level of crops according to the AB-DTPA extractable soil test (Havlin and Soltanpour, 1981). Whereas Cr, Cd, Ni, and Pb were within the permissible limits for plants.

3.2.2. AB-DTPA extractable heavy metals

Soil test for heavy metals content alone is not the only indication of the heavy metal contamination of a soil and the uptake of heavy metals can be highly variable between years (Truby and Raba, 1990). The heavy metal content of the soil was determined by AB-DTPA extraction method. The effect of amendments on each metal is described individually as under:

Physico-chemical properties of composite soil sample taken from the experimental plots.

Properties	Unit	Soil sample	
Sand	%	49.1	
Silt	%	39.4	
Clay	%	11.5	
Textural class	_	Loam soil	
Organic matter	%	1.08	
Lime content	%	9.04	
рН	_	8.3	
EC	$dS m^{-1}$	0.32	
Р	${ m mgkg^{-1}}$	17.51	

3.2.2.1. Cadmium (Cd). The results for AB-DTPA extractable Cd concentration in soil receiving different amendments and irrigated with wastewater showed significant variation (P < 0.05) among the different amended plots. The Humic acid treated plot had the maximum Cd content determined in the AB-DTPA extractable soil test which was followed by un-amended wastewater treated plot (Fig. 1).

The overall treatment effect was significant to control but nonsignificant among the treatments. Relatively higher concentration of Cd was noted in the post-harvest soil from all the treated plots. The addition of PM resulted in the decrease of Cd content in soil which was comparable to all the other treatments. Bolan et al. (2003) reported that addition of bio-solid compost reduced the mobility of Cd in soil. DAP also showed a reduction in the mobility of Cd in soil confirming the results of Zwonitzer et al. (2002) and Bolan and Duraisamy (2003), who reported the superiority of lime and P sources on reducing the mobility 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.

The reason of elevated level of Cd in the wastewater treated plot, apart from being taken control, may also be due to the buildup of the metal overtime because of the use of the same design in the series of studies and long application of wastewater as a source of irrigation in the same plot. As per the criteria of toxicity of Cd described by Linzon (1978), the concentration of Cd was below the level to cause toxicity to plants at this stage.

3.2.2.2. Chromium (Cr). The addition of amendments had a significant effect (P < 0.05) on the AB-DTPA extractable Cr in soil as compared to control, whereas there was not much addition of Cr with the addition of waste water since there was no significant difference between the pre-sowing and post-harvest soil analysis (Fig. 2). The highest concentration of Cr was noted in the un-amended wastewater plot, while the lowest was noted in Tube-well water irrigated plots. All the treatments were comparable (P < 0.05) among themselves in stabilizing the concentration of Cr in soil.

Among other amendments, the application of both FYM and HA showed a trend in reducing the extraction of Cr during analysis, indicating its superiority over inorganic amendments in stabilizing Cr. The effectiveness of organic amendments in reducing the mobility of Cr in contaminated soils has been reported by Bolan and Duraisamy (2003).

3.2.2.3. Copper (Cu). The addition of different organic and inorganic amendments to the soil irrigated with wastewater from the Malakandhere drain significantly (P < 0.05) decreased the bioavailability of AB-DTPA extractable Cu in soil compared to the control, but the decrease was comparable among the treatments (Fig. 3). The concentration of Cu ranged from 4.68 mg kg⁻¹ in the un-amended wastewater irrigated plot to 3.58 mg kg⁻¹ in DAP amended plot. Even though non-



Fig. 1. Graph representing AB-DTPA extractable Cd (mg $\rm kg^{-1}$) in soil treated with various amendments.



Fig. 2. Graph representing AB-DTPA extractable Cr ($mg kg^{-1}$) in soil treated with various amendments

significant. DAP was more effective in stabilizing Cu in soil. With alkaline pH and calcareous nature of the soil, the concentration of Cu in soil remained under the threshold level as the extractability of Cu is governed by soil pH, lime and organic matter content of soil. Khan and Jones (2009) reported that Cu extractability was reduced over time in soil treated with green compost and lime. DAP enhanced the extractability of Cu and the reason of the enhance 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 formation of soluble Cu phosphate species might have caused the increase in solubility of Cu in their study.

Comparing the critical soil test values of Cu described by Linzon (1978), the soil of all the amended plots analyzed showed that the Cu level is not high enough to cause phyto-toxicity. Consistent irrigation with wastewater for a longer period of time may cause potential buildup of the metal in soil, which can cause problem over the years.

While comparing the pre-sowing and post-harvest Cu content of the soil, it was found that there were significant differences and higher values were found in the post-harvest soil samples indicating its buildup in the soil.

3.2.2.4. Iron (Fe). The application of amendments to the soil had a more pronounced effect on the levels of AB-DTPA extractable Fe (Fig. 4) compared to all other amendments which were statistically similar to control (P < 0.05) compared to pre-sowing except wastewater alone application. Organic amendments; PM, FYM, and HA, were able to significantly reduced the Fe content in post-harvest soil samples.

The overall result showed that the Fe content in soil was above the critical level of crop requirements (Havlin and Soltanpour, 1981) but below the excessive range to be considered 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).



Fig. 3. Graph representing AB-DTPA extractable Cu (mg kg⁻¹) in soil treated with various amendments



Pre-sowing

Fig. 4. Graph representing AB-DTPA extractable Fe (mg kg^{-1}) in soil treated with various amendments.

Comparing the pre-sowing and post-harvest soil test for Fe, there has been irregular decrease of Fe in almost all the treatments. Turby and Raba (1990) reported that the concentration of heavy metals is highly variable between years and may increase or decrease under different conditions.

3.2.2.5. Manganese (Mn). The concentration of AB-DTPA extractable Mn varied significantly (P < 0.05) and the highest value (18.48 mg kg⁻¹) was noted in wastewater irrigated plot, although the differences in the treatments were non-significant among themselves (Fig. 5). The addition of TSP proved better in reducing the extractability of Mn in soil, which was comparable to FYM. This behavior might be due to the formation of Mn-insoluble complexes formed by the addition of TSP.

Francisco et al. (2006) reported that the addition of urban waste compost to barley reduced Mn concentration in the dry matter indicating its stability in soil.

Sabir et al. (2008) in their incubation studies reported reduction of Mn with addition of activated carbon but AB-DTPA extractable Mn increased with FYM and PM. It was further noted that addition of PM increased AB-DTPA extractable Mn content in soil (Fig. 5).

By comparing the pre-sowing Mn content with post-harvest content, no significant differences are observed in any of the treatments although higher values were recorded in the post-harvest soil sample indicating the buildup of Mn in soil.

3.2.2.6. Nickle (Ni). Analysis of the soil samples for the concentration of Ni after the application of different organic and inorganic amendments showed that significant (P < 0.05) difference among the treatments and control (Fig. 6), while the treatments showed similar behavior among themselves. The highest concentration of Ni was noted in wastewater irrigated plot. DAP proved better in reducing the extractability of Ni, which was followed by FYM and comparable to TSP. The wastewater



Fig. 5. Graph representing AB-DTPA extractable Mn (mg kg⁻¹) in soil treated with various amendments.



Fig. 6. Graph representing AB-DTPA extractable Ni (mg $\rm kg^{-1})$ in soil treated with various amendments.

and tube-well water had the highest and lowest value of 0.90 mg kg $^{-1}$ and 0.54 mg kg $^{-1}$, respectively.

The significant reduction in Ni concentration by TSP may be due to the presence of Ca that has reduced its bioavailability. Sabir et al. (2008) reported increase in Ni concentration with the addition of FYM and activated carbon. The significant reduction in Ni extractability in poultry manure amended plot may be because of the formation of insoluble Ni and organic matter complexes, as reported by various researchers (Halim et al., 2003; Karaca, 2004). A comparison of the values with the criteria described by Linzon (1978) suggests that the concentration of Ni was not high enough to cause phytotoxicity. The results are also in agreement with the findings on Bano (2004).

A comparison of the pre- and post-harvest Ni concentration in soil indicates buildup of the metal in soil, which is not significant at this stage but may cause potentially hazardous level of buildup over a period of time. The long term use of wastewater without the use of amendments is, therefore, advocated to be monitored.

3.2.2.7. Lead (Pb). The addition of amendments to soil had a significant (P < 0.05) effect on the AB-DTPA extractable Pb content of soil while the effect of sampling time was not significant. DAP amended plot was the most effective in stabilizing Pb in soil, which was comparable to all other treatments. The highest concentration was noted in untreated wastewater applied plot. While the minimum value (1.99 mg kg⁻¹) was shown by tube well water applied plot.

Phosphate amendments were more effective in stabilizing Pb in soil and a decrease in the soil content was noted in DAP amended plot which was most effective in stabilizing Pb in soil. The reduction level shown by TSP was at par with DAP, but because of the initially high concentration of the metals, the reduction was lesser than the former. The maximum concentration was noted in wastewater applied plot (Fig. 7). Organic amendments did not show promising results in lowering the concentration of lead in soil.



Fig. 7. Graph representing AB-DTPA extractable Pb (mg $\rm kg^{-1})$ in soil treated with various amendments.

These results are 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 (PbSO₄) 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 hydroxy pyromorphite [Pb(PO₄)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.

According to Swein and Mitchell (1978), Pb concentration of soil can range from 2 to 200 mg kg⁻¹ with an average value of 20 mg kg⁻¹. Comparing the concentrations determined in this study with Kabata-Pendias and Pendias (1985) standard indicates that the concentration of Pb was very low and is not likely to cause any problems.

3.2.2.8. Zinc (Zn). Results of the various organic and inorganic amendment treatments on Zn in soil followed the same trend as was noted for all other metals under study but were slightly different than Mn. There were significant differences in Zn concentration, compared to control, when wastewater was supplemented with organic and inorganic amendments (Fig. 8). Higher Zn content was noted in waste water applied plots which was followed by FYM plot whereas significantly lower values were recorded in tube-well water irrigated plots. The addition of amendments did not show a visible effect on the AB-DTPA extractable Zn content. DAP was more effective in reducing its extractability.

The results are in accordance with the findings of Shuman (1999), who reported that the retention of Zn by soil increased in the presence of organic materials. Similar results were reported by Sabir et al. (2008).

3.3. Plant biomass

The crop was harvested thrice. Results indicated that the shoot biomass was significantly affected by the irrigation water supplies and different amendments (Fig. 9). Tube-well water irrigation resulted in the production of minimum biomass as compared to wastewater irrigation with an increase of 20% fresh biomass in wastewater as compared to tube-well water. The increase in fresh biomass, produced by the addition of amendments (both organic and inorganic) was non-significant (among themselves) but an increase of 35% was recorded against control (tube-well water) for HA, 32% for DAP, 31% for PM, 31% for FYM and 29% for TSP, which indicates the nutritive value of wastewater and amendments. The maximum biomass was produced in HA (2.38 kg) applied plots and irrigated with wastewater, with an increase of 35% over control-I (Tube-well water: 1.93 kg). Haroon (2009) reported 27% increase in the yield of wheat due to 1 kg Humic acid addition. Humic acid is thought to improve yield due to its capacity of supplying N & P to plants but the total amount of HA added is generally 1 to 2 Kg ha^{-1} which will hardly supply 0.04 to 0.08 kg N and



Fig. 8. Graph representing AB-DTPA extractable $Zn \ (mg \ kg^{-1})$ in soil treated with various amendments.



Fig. 9. Graph representing fresh biomass production over three cuts as affected by various amendments.

0.001 kg ha⁻¹ P to soil. This amount is far below the nutrient requirements of plants (Khattak and Mohammad, 2008; Sharif et al., 2002b). However, the beneficial effect may be associated with the improvement in the physico-chemical and biological environment of soil (Brannon and Sommers, 1985). Ben Rebah et al. (2002) reported increase in alfalfa yield when irrigated with sewage sludge. Segura et al. (2004) also advocated the reuse of wastewater in arid and semi-arid regions of the world. The investigation of (Jamali et al., 2007) also highlights the increased danger of growing vegetables in the agriculture land, continuously irrigated and dressed with waste water and sewage sludge.

4. Conclusions

Although the use of wastewater can increased the yield by 20% which was further increased by the addition of amendments, the health risks associated with the use of untreated wastewater cannot be overlooked. The concentration of heavy metals in the untreated wastewater applied plot showed a buildup of all the heavy metals which were considerably higher than the tube-well water applied plots and treated plots. Although at this stage the level of metals was within the permissible limits of WHO standard, however, there is a potential risk for using untreated wastewater for long period without addition of amendments or growing crops that are less accumulator of metals. Among the different amendments it was noted that DAP was effective in reducing the mobility of Zn, Cu, and Pb where as FYM was better for reducing the availability of Cr, Fe, Mn, Ni and Pb. In the light of the present study, it is therefore recommended that both DAP and FYM should be used at 120 kg P ha⁻¹ and 10 t ha⁻¹ where untreated wastewater is applied directly to irrigate crops.

Acknowledgments

The authors are grateful to the Higher Education Commission (Grant No. 162) Pakistan for funding the research and The University of Agriculture Peshawar, Pakistan for providing laboratory and field facilities for the current research.

References

- Bano, D., 2004. Spatial and Temporal Variation of Heavy Metals in Industrial Effluents of Hayatabad and its Effect on Soil M. Sc. (Hons) Thesis Dept. Soil and Environ. Sci. NWFP Agric. Univ. Peshawar, Pakistan.
- Basta, N.T., McGowen, S.L., 2004. Evaluation of chemical immobilization treatments for reducing heavy metal transport in a smelter-contaminated soil. Envir. Pollut. 127, 73–82.
- Ben Rebah, F., Prevost, D., Tyagi, R.D., 2002. Growth of alfalfa in sludge-amended soils and inoculated with rhizobia produced in sludge. J. Environ. Qual. 31, 1339–1348.
- Boisson, J., Ruttens, A., Mench, M., Vangronsveld, J., 1999. Evaluation of hydroxyapatite as a metal immobilizing soil additive for the remediation of polluted soils: I. Influence of hyroxyapatite of metal exchangeability in soil, plant growth and plant metal accumulation. Environ. Pollut. 104, 225–233.

- Bolan, N.S., Duraisamy, D., 2003. Role of inorganic and organic soil amendments on immobilisation and phytoavailability of heavy metals: a review involving specific case studies. Aust. J. Soil Res. 41, 533–555.
- Bolan, N.S., Adriano, D.C., Curtin, D., 2003. Soil acidification and liming interactions with nutrient and heavy metal transformation and bioavailability. Adv. Agron. 78, 215–272.
- Brannon, C.A., Sommers, L.E., 1985. Preparation and characterization of model humic polymers containing organic P. Soil Biol. Biochem. 17, 213–219.
- Chen, Y.X., Lin, Q., Luo, Y.M., He, Y.F., Zhen, S.J., Yu, Y.L., Tian, G.M., Wong, M.H., 2003. The role of citric acid on the phytoremediation of heavy metal contaminated soil. Chemosphere 50, 807–811.
- Chiu, K.K., Ye, Z.H., Wong, M.H., 2006. Growth of Vetiveria zizanioides and Phragmites australis on Pb/Zn and Cu mine tailings amended with manure compost and sewage sludge: a greenhouse study. Bioresour. Technol. 97, 158–170.
- Drechsel, P., Christopher, A.S., Raschid-Sally, L., Redwood, M., Bahri, A., 2010. Wastewater Irrigation and Health (Assessing and Mitigating Risk in Low-income Countries). Earthscan Publications Ltd., p. 440.
- Ensink, J.H.J., Simmons, R.W., Van der Hoek, W., 2004. Wastewater use in Pakistan: the case of Haroonabad and Faisalabad. Scott et al., Wastewater Use in Irrigated Agriculture Confronting the Livelihood and Environmental Realities. A joint CABI/IWMI/IDRC publication.
- Francisco, G.L., Mariano, A., Alfredo, P., 2006. Phytoavailability and Fractions of Iron and Manganese in Calcareous Soil Amended with Composted Urban Wastes. J. Environ. Sci. Health (B) 41 (7), 1187–1201.
- Gee, G.W., Bauder, J.W., 1986. Particle size analysis, 383–411. In: Klute, A. (Ed.), Methods of Soil Analysis. Part 1. Physical and Mineralogical Methods, 2nd ed. Agron. Monogram 9. ASA and SSSA, Madison, WI.
- Ghosh, A.K., Bhatt, M.A., Agrawal, H.P., 2012. Effect of long-term application of treated sewage water on heavy metal accumulation in vegetables grown in northern India. Environ. Monit. Assess. 184 (2), 1025–1036.
- Halim, P.M., Conte, Piccolo, A., 2003. Potential availability of heavy metals to phytoextraction from contaminated soils induced by exogenous humic substances. Chemosphere 52 (1), 265–275.
- Haroon, 2009. Increasing crop production through humic acid in salt affected soils. Ph.D Dissertation Submitted to Dept. of Soil and Environmental Sciences. NWFP Agricultural University Peshawar.
- Havlin, J.L., Soltanpour, P.N., 1981. Evaluation of the AB-DTPA soil test for Fe, Zn, Mn, Cu. Soil Sci. Soc. Am. J. 45, 55–70.
- Hettiarachchi, G.M., Pierzynski, G.M., 2002. In situ stabilization of soil lead using phosphorous and manganese oxide: influence on plant growth. J. Environ. Qual. 31, 564–572.
- Hooda, P.S., Alloway, B.J., 1996. The effect of liming on heavy metal concentrations in wheat, carrots and spinach grown on previously sludge applied soils. J. Agric. Sci. 127, 289–294.
- Huibers, F.P., Moscoso, O., Duran, A., Lier, J.B.V., 2004. The Use of Waste Water in Cochabamba, Bolivia: a Degrading Environment. IDRC Books Free online (http:// www.idrc.ca).
- Jamali, M.K., Kazi, T.G., Arain, M.B., Afridi, H.I., Jalbani, N., Memon, A.R., 2007. Heavy metal contents of vegetables grown in soil, irrigated with mixtures of wastewater and sewage sludge in Pakistan, using ultrasonic-assisted pseudo-digestion. J. Agron. Crop Sci. 193 (3), 218–228.
- Kabata-Pendias, A., Pendias, H., 1985. Trace elements in soil and plants, pp. 57-59.
- Kanwar, J.S., Sandha, M.S., 2000. Waste water pollution injury to vegetable crops, a review. Agric. Rev. 21 (2), 133–136.
- Karaca, A., 2004. Effect of organic wastes on the extractability of cadmium, copper, nickel and zinc in soil. Geoderma. 122, 297–303.
- Kennish, M.J., 1992. Ecology of Estuaries: Anthropogenic Effects. CRC Press, Boca Raton.
- Khan, M.J., Jones, D.L., 2008. Chemical and organic immobilization treatments for reducing phytoavailability of heavy metals in copper mine tailings. J. Plant Nutr. Soil Sci. 171, 908–916.
- Khan, M.J., Jones, D.L., 2009. Effect of compost, lime and DAP on the phytoavailability of heavy metals in copper mine tailing soils. Pedosphere 19, 631–641.
- Khan, S., Cao, Q., Zheng, Y.M., Huang, Y.Z., Zhu, Y.G., 2008. Health risks of heavy metals in contaminated soils and food crops irrigated with wastewater in Beijing, China. Environ. Pollut. 152 (3), 686–692.
- Khattak, R.A., Mohammad, D., 2008. Increasing crop production through humic acid in rainfed and salt affected soils in Kohat Division. Final Technical Report (2004–2007). Department of Soil and Environmental Sciences, NWFP Agricultural University, Peshawar, Pakistan.
- Kirkham, M.B., 1983. Problems using wastewater on vegetable crops. Hortic. Sci. 21, 24–27. Laperche, V., Logan, T.J., Gaddam, P., Traina, S.J., 1997. Effect of apatite amendments on plant uptake of lead from contaminated soil. Environ. Sci. Technol. 31, 2745–2753.
- Linzon, S.N., 1978. Phytotoxically excessive levels for contaminants in soil and vegetation. Report of ministry of the Environment. Ontario, Canada.
- Ma, Q.Y., Logan, T.J., Traina, S.J., 1995. Lead immobilization from aqueous solutions and contaminated soils using phosphate rocks. Environ. Sci. Technol. 29, 1118–1126.
- McGowen, S.L., Basta, N.T., Brown, G.O., 2001. Use of Diammonium phosphate to reduce heavy metal solubility and transport in smelter contaminated soil. J. Envir. Qual. 30, 493–500.
- Nelson, D.W., Sommer, L.E., 1982. Total carbon, organic carbon and organic matter. In: Page, A.L. (Ed.), Methods of Soil Analysis: Chemical and Microbiological Properties. Part 2, 2nd ed. Agronomy, Madison, WI, USA, pp. 539–577.
- Pierzynski, G.M., Sims, J.T., Vance, G.F., 2000. Soil phosphorus and environmental quality. In Soils and Environmental Quality. CRC Press, Boca Raton, pp. 155–207.
- Qadir, M., Wichelns, D., Raschid-Sally, L., McCornick, P.G., Drechsel, P., Bahri, A., Minhas, P.S., 2008. The challenges of wastewater irrigation in developing countries. Agric. Water Manag. 97 (2010), 561–568.

Richard, L.A., 1954. Diagnosis and Improvement of Saline and Alkali Soil. USDA Handbook 60, Washington D.C.pp. 124–128.

- Sabir, M., Ghafoor, A., Saifullah, M.Z., Rehman, Murtaza, G., 2008. Effect of organic amendments and incubation time on extractability of Ni and other metals from contaminated soils. Pak. J. Agric. Sci. 45, 18–24.
- Scott, C., Faruqui, N.I., Raschild-Sally, L., 2004. Wastewater Use in Irrigated Agriculture: Confronting the Livelihood and Environmental Realities. A Joint CABI/IWMI/IDRC Publication.
- Segura, M.L., Grandos, M.R., Moreno, J., Urrestarazu, M., 2004. Response of greenhouse melon and tomato crops to wastewater irrigation. Acta Horticult. 633, 391–396.Sharif, M., Khattak, R.A., Sarir, M.S., 2002. Wheat yield and nutrients accumulation as
- affected by humic acid and chemical fertilizers. Sarhad J. Agric. 18, 323–329.
- Shuman, L.M., 1999. Organic waste amendments effect on zinc fractions of two soils. J. Envir. Qual. 28, 1442–1447.
- Smith, J.L., Doran, J.W., 1996. Measurement and use of pH and EC for soil quality analysis. Methods for Assessing Soil Quality. Soil Science Society of America, Madison WI.
- Swein, D.J., Mitchell, R.I., 1978. Trace elements distribution in soil profile. J. Soil Sci. II 347–368.
- Steel, R.G.D., Torrie, J.H., 1980. Principles and Procedures of Statistics. A Biometrical Approach. 2nd edition. McGraw-Hill, New York, N.Y., p. 633.
- Truby, P., Raba, A., 1990. Heavy metal uptake by garden plants from Freiburg sewage farm wastewater. Agribiol. Res. Stud. 43, 139–146.

- Ullah, H., Khan, I., Ullah, I., 2011. Impact of sewage contaminated water on soil, vegetables and underground water of peri-urban Peshawar, Pakistan. Environ. Monit. Assess. 184 (10), 6411–6421. http://dx.doi.org/10.1007/s10661-011-2429-4.
- USEPA, 1998–1999. Secondary contaminants levels: recommended maximum concentration of heavy metals and inorganic constituents in water. Final Rule. Federal Register 56 (110). US Environment Protection Agency, pp. 26410–26564.
- Wong, M.H., Lau, W.M., 1985. The effects of applications of phosphate, lime. EDTA. refuse compost and pig manure on the lead contents of crops. Agric. Wastes 12, 61–75.
- Wong, M.H., 2003. Comparison of several solid wastes on the growth of vegetable crops. Agric. Ecosyst. Environ. 30 (1–2), 49–60.
- Xardalias, C., Kalavrouziotis, I.K., Koukoulakis, P.H., Papadopoulos, A., Fourniotis, N.Th., 2013. The effect of zeolites on heavy metal phytoavailability to *Raphanus sativus*, L. in the presence sludge. Fresenius Environ. Bull. 22 (8), 2344–2349.
- Zwonitzer, J.C., Pierzynski, J.C., Hettiarachchi, G.A., 2002. Effect of phosphorus additions on lead, cadmium and zinc bio-availabilities in a metal-contaminated soil. Water Air Soil Pollut. 143, 193–209.