Journal of Geochemical Exploration 159 (2015) 1–7

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

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.

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

http://dx.doi.org/10.1016/j.gexplo.2015.07.002
0375-6742/

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), molybdenum (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 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.

Table 1
Nature and rate of amendments application to 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}

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 physico-chemical 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 ($CaCO_3$ = 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 (±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.