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Original Research Article

Impact of Tannery Effluent on Bioaccumulation of Heavy Metals Concentration in Maize Grains (*Zea mays* L.)

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ABSTRACT

Tannery effluents adversely affect the growth and development of crops when they are used for irrigation. Therefore, this study was carried out to assess the bio-accumulation of heavy metal on maize grains of selected varieties (BHQPY545 and Malkesa-2) using different effluent treatments. The treatments were made by mixing measured quantities of tannery effluent in distilled water, i.e. 0, 25, 50, 75 and 100%. The experiment was carried out in a completely randomized design with five effluent treatments, each replicated three times. The effluent is a dark bluish green in color with a high biological oxygen demand (182mg/kg) along with much higher concentrations of total suspended solids (13,100 mg/kg) and total dissolved solids (3000 mg/kg), but the concentrations of some metals were found the under the normal range recommended by Food and Agriculture Organization and United Nations Environmental Protection Agency. Tannery effluent was tested for its effect on maize greenhouse conditions. The result of the study indicates that chromium had the highest concentrations in the tannery effluent, while Zn had the least concentrations. The metal concentrations in effluent samples were in the order of Cr > Pb > Fe > Cd > Cu > Zn. The accumulation of heavy metal results showed that Fe was detected in the highest concentration, followed by Cr for all treatments in both varieties of maize. The sequence of metal accumulation in decreasing order was: Fe > Cr >Zn > Cu > Cd >Pb in the maize seeds. In both selected varieties, in the lower treatments (T1 and T2), the concentration of all heavy metals was very low compared to T4 although it exceeded the permissible limits, except for Cu and Zn. Finally, it is understood that effluent treated plant may lead to adverse health outcomes upon human consumption.

Keywords: Fungi, Root length, Soil parameter

INTRODUCTION

Industries release different types of pollutants such as heavy metals, resin pellets, organic toxins, oils, nutrients, and solids into their wastewater. These pollutants affect the quality of soil, water, and air, which leads to many diseases (Huma et al. 2012). The distilleries, like detergent, chemical factories, textile dyeing industries, tanneries, electroplating, sugar mills, pulp and paper mills, pharmaceuticals, and dairy industries are major effluent discharging industries. In these industries, serious pollution problems are created by tanneries. The leather tanning process is one of the most polluting activities, and also has one of the highest toxic intensities per unit of output, because converting hides into leather involves several chemically intensive processes/stages. All stages consume high quantities of water and use large amounts of chemicals. The release of effluents without proper treatment into the nearby rivers, irrigation canals, and streams adjacent to agricultural fields causes serious hazards, intensifying the adverse effects on ecosystems like water, soils, and plants (Shukry 2001).

In Ethiopia, the tannery industry is one of the major foreign currency-earning resources. Subsequently, during the past 20 years, the industries have had substantial government support and increased in numbers throughout the country. Moreover, the tanning industry involves mechanical changes which use a lot of water and chemical reactions. Chemical reactions, have adverse effects on the environment and human health. Most of the time, it is, in developing countries, discharged into rivers or other water areas or onto open field land (Favazzi 2003).

An extensive amount of water is consumed by the tannery industry for the processing of hides. For 1kg of hide the requirement is 50-60 liters of water (Indira and Ravi 2006). The discard of these wastes causes serious problems because effluents of tannery without treatment have high chemical oxygen demand (COD), biological oxygen demand (BOD), and high quantities of alkaline salts such as sulfide, chromium, and chloride (Bajza and Vrcek 2001). Moreover, effluents from tanning industries containing Cr and other metals are discharged into the local water bodies which are used for irrigation purposes. Mostly, tannery effluent water is unsuitable for crop growth due to the presence of chromium beyond the tolerance limit (< 2 ppm). The high level of Cr and nutrient

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contents in the effluent has been reported to inhibit seed germination and seedling growth, which might be due to the presence of excessive amounts of dissolved solids, chlorides, sulfides, and chromium.

In Ethiopia, the best examples of polluted water bodies are from tannery tributaries of the Awash river, such as the Akaki, Kaliti, and Modjo rivers. Occupants around the river and /or the tannery reported the death of their cattle, the drying up of green plants, and the bad smell that resulted due to the death of organisms and the action of microorganisms and finally led to causes of diseases. However, the demand for irrigation water supply, farmlands nearby to tanneries are habitually irrigated with poor-quality water (Eskindir 2011). In several arid and semiarid regions, water shortage is a limiting factor. The farmers near tannery industries are forced to use the tannery effluents for irrigation purposes (Rajendra et al. 2010). The effect of various industrial effluent and heavy metal elements on crop plants has gained the attention of many researchers (Rahman et al. 2002). However, the influence of tannery effluent on the accumulation of heavy metals in Maize seed has not been reported in Ethiopia. Therefore, the research was initiated to determine the selected heavy metal concentration in Maize seed irrigated with diluted tannery effluent.

MATERIALS AND METHODS

Collection of maize seed and preparation of effluent for treatments

Plant Materials: The selection of the crop plant was based on its economic importance as well as availability in (HU) Ethiopia. Accordingly, two available varieties of Maize BHQPY545 and Malkesa-2 were used in this study. The effluents were collected directly from the outlet of Modjo tannery (East Showa, Oromia region, Ethiopia) in plastic containers and prepared with different treatments. Different treatments of tannery effluent were made by mixing with distilled water with the following percentage for bioassay and greenhouse studies. T0 (100% distilled water control), T1 (25% effluent + 75% distilled water), T2 (50% effluent + 50% distilled water), T3 (75% effluent + 25% distilled water), and T4 (100% effluent).

Physicochemical analysis of tannery effluent

The selected physicochemical properties of untreated tannery effluent were analyzed by the standard method of analysis as per the guidelines of the American Public Health Association (APHA 1998). pH was determined by the pH meter, EC (Electrical conductivity) by the EC meter, TDS (Total dissolved solids) by gravimetric method, BOD (Biological oxygen demand) by dissolved oxygen meter (incubator), and AAS (atomic absorption spectrophotometer) was used to determine heavy metals such as Cd, Cr, Cu, Fe, Pb, and Zn. To determine the presence of heavy metals in the collected effluent samples, 100ml of each of the effluent samples was filtered using Whatman No. 1 filter paper and then transferred into beakers containing 10ml of concentrated HNO3. The samples were boiled slowly and then evaporated on a hot plate to the lowest possible volume (about 20ml). The beakers were allowed to cool and another 5ml of concentrated HNO3 was added. Heating was continuous with the addition of concentrated HNO3 as necessary until digestion was complete. The samples were evaporated again to dryness (but not baked) and the beakers were cooled, followed by the addition of 5ml of HCl solution. The solutions were then warmed and 5ml of NaOH was added, then filtered. The filtrates were transferred to 100ml volumetric flasks and diluted to the mark with distilled water. The solutions were then used for elemental analysis. A total of six metallic elements, Cd, Cr, Cu, Fe, Pb, and Zn were determined.

Greenhouse experiments

Seeds were surface sterilized with antifungal 15% sodium hypochlorite for two minutes and then washed with distilled water several times to remove the sodium hypochlorite. Three surface sterilized seeds were sown in plastic pots filled with an equal amount of soil (1:1:1 garden soil, cow dung manure, and sand); in a greenhouse using CRD design with three replications along with their respective controls. The experimental plants were treated with 1000 ml of respective tannery effluent (25%, 50%, 75%, and 100%) every 3 days after 5th leaf emergence (17th day after sowing), and the control was treated with normal water. All the plants were grown under greenhouse conditions at Haramaya University.

Determination of heavy metal accumulation of maize seeds

A total of 5 grams of seed samples of selected varieties of maize from each of the five effluent treatments were collected from the greenhouse in Rarre station and transported to the central laboratory of Haramaya University for the determination of heavy metal in the seeds. Samples were analyzed for heavy metals, copper (Cu), chromium (Cr), cadmium (Cd), iron (Fe) and lead (Pb), and zinc (Zn) using atomic absorption spectrophotometer (AAS) by the method followed by Girmaye (2014). Accordingly, the sample was washed with distilled water to eliminate suspended particles and then dried on a sheet of paper to eliminate excess moisture and carefully dried in the oven at 70oc for 24h. Five grams of each sample were weighed and crushed by a grinder followed by wet digestion with HNO3 and H2O2 at a ratio of 3:1. The samples were digested on an electric hot plate for 4h at 80-90 oc at which the samples were made to boil and digestion was continued until a clear solution was obtained. It was then cooled, followed by the addition of 5 ml of HCl solution. After cooling, the solution was filtered through Whatman No.1 filter paper. Then they transferred to a 25 ml volumetric flask by adding distilled water. Finally, the filtrate was analyzed for heavy metal content using atomic absorption spectroscopy.

Data analysis

Analysis of variance was done to compare the treatments with the control. Each experiment was performed in triplicates and treatments, meaning, standard errors were calculated from the data obtained for various parameters of growth, germination percentage, and yield experiments using SAS software. Mean separation was done by using the least significant difference (LSD) at a 5% level of significance.

RESULTS AND DISCUSSION

Physicochemical characteristics of tannery effluent

The physicochemical parameters such as color, odor, pH, BOD, EC, total dissolved solids, total suspended solids, and total solids were analyzed and the results are indicated in table 2 with the maximum concentration recommended for crop production (FAO, 1985 and USEPA, 2012).

Table 1. Physicochemical characteristics of tannery effluent.

Parameters	Unit	Values	Standard set for crop production
Color	-	Dark bluish green	-
Odor	-	Pungent (offensive)	-
pH	-	5.88	6-9
BOD	mg/L	182	<30
EC	*µS/cm*	13,090	<3,000
TDS	mg/L	13,100	<2000
TSS	mg/L	3,000	<30
TS	mg/L	16,100	-

The tannery effluent used in this study was dark blueish-green. This may be due to the presence of high TSS and TDS. Kambole (2003) reported that the high color detected could be attributed due to high TSS and TDS. The dark bluish-green color of the effluent is a major problem for the natural environment. It reduces light penetration in water bodies, which in turn affects aquatic life (Pazouki et al. 2008). The odor of the effluent was pungent. The offensive odor of effluent is due to the reduction of sulfate compounds to hydrogen sulfide by sulfate-reducing bacteria (Mahimaraja and Bolan 2004). The effluent was acidic with the pH recorded as 5.88. Kohli and Malaviya (2013) reported that raw tannery effluent was acidic with a pH of 3.61. However, a report from different investigations has shown the basic nature of tannery effluents (Aklilu et al. 2012; Mandakini and Khillare 2016). The acidic pH of the tannery effluent may be due to the presence of a high concentration of chrome, which is in line with Reddy et al. (2014) who reported that chrome effluent is highly acidic. The pH obtained was lower than the permissible level for crop production (USEPA 2012).

The effluent contains a much higher amount of total dissolved solids, suspended solids, electrical conductivity, and BOD than that of the limit prescribed by FAO (1985) and USEPA (2012). The electrical conductivity value of the tannery effluent recorded was 13090µS/cm. Likewise, the higher electrical conductivity of tannery effluent was reported by Aklilu et al. (2012). The higher electrical conductivity of the effluent is due to the presence of a high concentration of dissolved salts in the effluent (Bhasin et al. 2007). Determination of BOD is one of the important parameters used in water pollution to evaluate the impact of wastewater on receiving water bodies. The value obtained for BOD was 182 mg/L. Aklilu et al. (2012) also reported higher amounts of BOD (147.29 mg/L), which is lower than the present report. In contrast to this study, Zereen et al. (2013) reported a much higher amount of BOD, which was 987 mg/L. An increase in BOD, which is a reflection of microbial oxygen demand, leads to depletion of DO which may cause hypoxia conditions with consequent adverse effects on aquatic biota (An et al. 2006). High values of BOD might be due to the presence of higher amounts of organic compounds in the effluents (Bhasin et al., 2007). The results obtained for TDS and TSS of effluent were 13100 and 3000 mg/L respectively. Kohli and Malaviya (2013) also reported higher amounts of TSS (1580 mg/L) which was lower than the recent study. However, Zereen et al. (2013) reported much higher amounts of TDS and TSS, which were 85500 mg/L and 2150 mg/L respectively. The presence of high levels of TSS and TDS may be due to the soluble and insoluble organic and inorganics present in the effluent (Nagarajan et al. 2005). The result of effluent analysis for those parameters shows conformity with the other studies (Aklilu et al. 2012; Mandakini and Khillare 2016).

Heavy metal analysis in tannery effluent

The heavy metal concentration of 100% (untreated) tannery effluent was presented in Table 3 and the results were compared to the standard prescribed for crop production (FAO, 1985 and USEPA, 2012). The result of the study indicates that chromium had the highest concentrations in the tannery effluent, while Zn had the least concentrations. The metal concentrations in effluent samples were in the order of Cr > Pb > Fe > Cd > Cu > Zn. The concentrations of heavy metals such as Cd, Cu, and Cr in the tannery effluent were above the maximum concentration recommended for crop production, while the concentrations Fe, Pb, and Zn are within the normal range recommended by FAO (1985) and USEPA (2012). Moreover, heavy metals such as copper, zinc, iron, and chromium are essential for the biochemical and physiological function of plants and animals in trace amounts (Nagajyoti et al. 2010). Higher concentration of heavy metals poses an adverse effect on plants as well as animals. Several researchers reported the effect of heavy metals on the plant. It has been revealed that high concentration of heavy metals affects the plant by inhibiting seed germination, seedling growth, root growth, shoot growth, and plant biomass (Aklilu et al. 2012; Zereen et al. 2013; Mandakini and Khillare 2016)

Table 2. Heavy metal concentrations in tannery effluent.

Heavy metals	Unit	Concentration in effluent	Standard set for crop production
Cadmium	mg/L	0.33	0.01
Copper	mg/L	0.22	0.20
Chromium	mg/L	2.74	0.10
Iron	mg/L	1.38	5
Lead	mg/L	1.50	5
Zinc	mg/L	0.12	2

Heavy metal accumulation of maize seeds

Figure (1-6) below shows the concentration of heavy metals in the seed of selected varieties of maize. The concentrations obtained for heavy metals were 17.83, 43.39, 103.47, 189.97, 15.59, and 47.09 in BHQPY545 and 23.35, 22.53, 109.29, 211.64, 21.47, and 53.12 in Malkesa -2 for Cd, Cu, Cr, Fe, Pb, and Zn respectively in 100% tannery effluent treatment. The concentrations of heavy metals were increased with increasing levels of treatment. The value obtained for both maize varieties is far above the value recommended by WHO/FAO (1976) for metals in foods and vegetables, except for Zn and Cu in malkes-2.

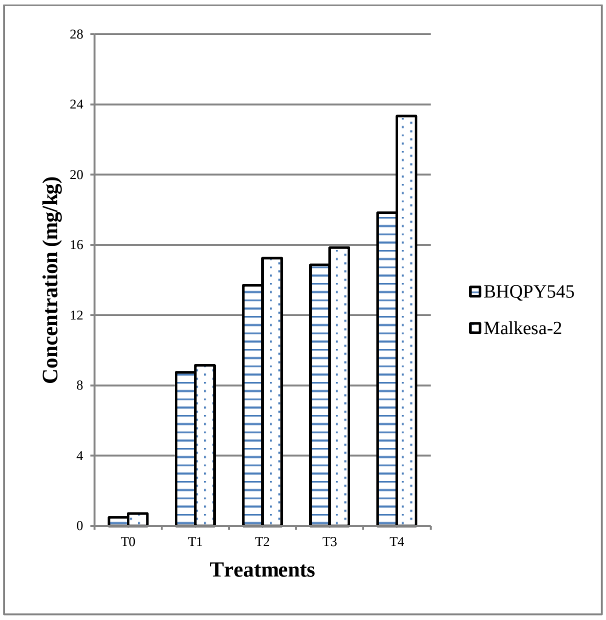

Fig 1. Concentration of cadmium.

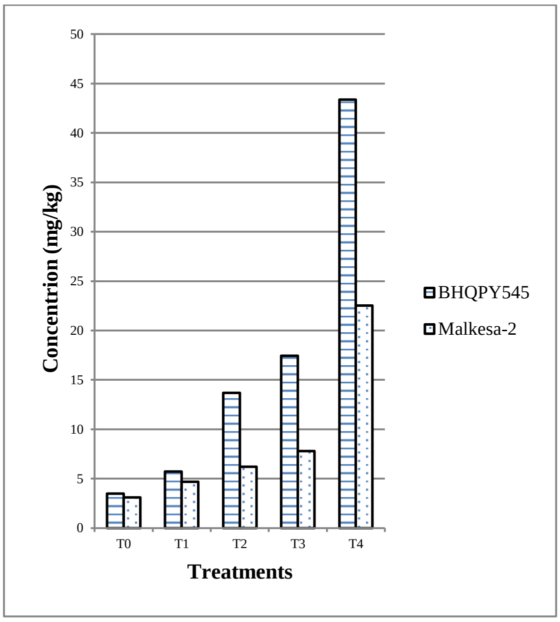

Fig 2. Concentrations of copper.

T0 = 100% tap water (control), T1 = 25% effluent + 75% tap water, T2 = 50% effluent + 50% tap water, T3 = 75% effluent + 25% tap water, T4 = 100% effluent, BHQPY545 and Malkesa-2 = Maize variety

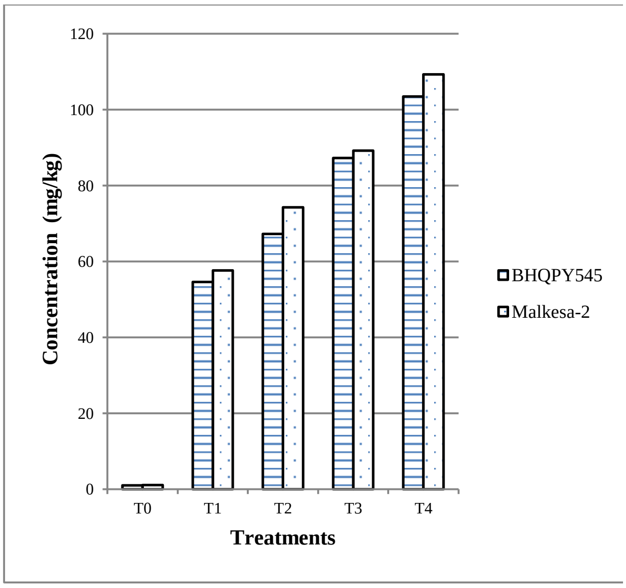

Fig 3. Concentration of chromium.

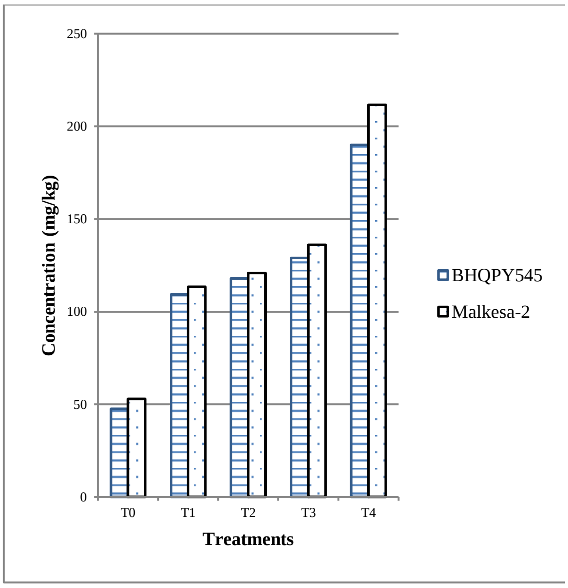

Fig 4. Concentrations of iron.

T0 = 100% tap water (control), T1 = 25% effluent + 75% tap water, T2 = 50% effluent + 50% tap water, T3 = 75% effluent + 25% tap water, T4 = 100% effluent, BHQPY545 and Malkesa-2 = Maize variety

The results showed that Fe was detected in the highest concentration followed by Cr for all treatments in both varieties of maize (Figure 4 and 5). The sequence of metal accumulation in decreasing order was: Fe > Cr >Zn > Cu > Cd >Pb in the maize seeds.

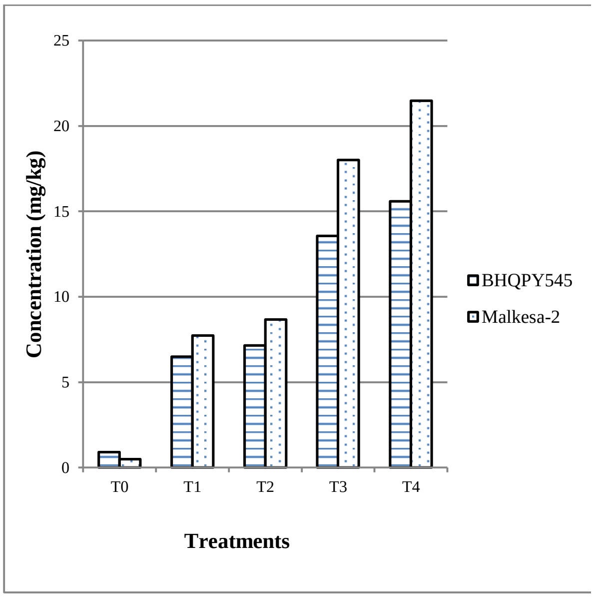

Fig 5. Concentration of lead.

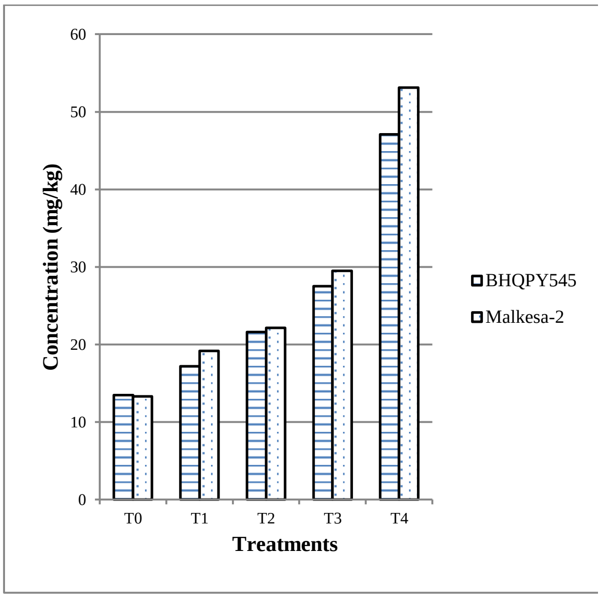

Fig 6. Concentrations zinc.

T0 = 100% tap water (control), T1 = 25% effluent + 75% tap water, T2 = 50% effluent + 50% tap water, T3 = 75% effluent + 25% tap water, T4 = 100% effluent, BHQPY545 and Malkesa-2 = Maize variety

In both selected varieties, at the lower treatments (T1 and T2), the concentration of all heavy metals was very low compared to T4 although it exceeded the permissible limits, except for Cu and Zn. In control (T0), the concentrations of all the heavy metals were found under normal recommended values by WHO/FAO for metals in foods and vegetables, with exception of Fe in Malkesa-2. This could suggest that tannery effluent has caused an increase in the heavy metal content of the maize compared to the control. The study indicates that all of the heavy metal concentrations in maize seeds were higher than the tannery effluent. Various researchers have reported elevated levels of heavy metals in sewage and tannery effluent irrigated crops (Singh and Kumar 2006; Mohammad Rusan et al. 2007). The results are in agreement with the finding of Gupta et al. (2010) who reported that concentrations of metals are lower in the tannery effluent and higher in the seed samples. Although the wastewater contains low levels of heavy metals, the plant samples showed higher values due to accumulation.

CONCLUSIONS

Finally, the study showed that the concentrations of heavy metals in maize seeds were increased with increasing levels of treatment. The results showed that Fe was detected in the highest concentration followed by Cr for all treatments in both varieties of maize. The sequence of metal accumulation in decreasing order was: Fe > Cr >Zn > Cu > Cd >Pb in the maize seeds. Among the metals studied, the accumulation of all heavy metals (Cd, Cu, Cr, Fe, and Pb) in maize seeds were above the maximum levels recommended by WHO/FAO for metals in foods and vegetables. Certain heavy metals are toxic to plants and humans when present above a certain limit. From the result, it is understood that effluent treated plant may lead to adverse health outcomes upon human consumption.

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