Physico-chemical Parameters of Soil and Heavy Metals Concentration in Vegetables Irrigated with Tin Mined Pond Water in Jos – South Plateau State

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Abstract

Irrigation of plants with tin mine pond water affects heavy metals in soil and vegetables and might cause major deleterious consequences on food safety and human health. Heavy metals in soil and vegetables in Jos – South Plateau State irrigated with tin mine pond water were estimated and compare with control levels of recent studies and the recommended tolerable limits. The experimental design was established to determine the accumulation of 8 heavy metals in two farm soils and vegetables grown and irrigated with tin mine pond water from each of the sites. Results shows that soil texture ranged from sand loamy to loamy sand, the pH slightly acidic 6.2, EC 11.5 – 13.3 dSm^{-1}, OM 5.60 – 5.90, g/kg CEC 19.0 – 21.2 meq, TN 10.2 g/kg, AP 8.8 g/kg, K 0.65 – 0.86 g/kg and Na 0.22 – 0. 57 g/kg. The concentration of metals in soil irrigated with mine pond water ranged from Pb 78.3 – 94.2, Cu 83.0 – 83.4, Cd 4.43 – 4.64, Zn 77.1 – 78.16, Cr 26.2 – 16.2, Fe 552 – 567, Mn 16.8 – 60.7 and As 125 – 146 mg/kg. The heavy metals investigated in vegetables from both farm A and B exhibited different ranges, Tomato 0.015 – 1.794 mg/kg, Garden Egg 0.001 – 1.174 mg/kg, Pepper 0.007 – 1.556 mg/kg, Cabbage 0.011 – 1.29 mg/kg, Carrot 0.010 – 1.59 mg/kg and Spinach 0.010 – 1.18 mg/kg. In the study it was observed that tin mine water used for irrigation of the soil vegetables increases the concentrations of the metals Pb, Cr, Cd, As and Mn in various degrees above the recommended standards WHO/FAO, 2010, EU, 2002.

Keywords: Irrigation, Heavy Metals, Tin – Mining, Vegetables

Paramètres Physico-Chimiques du Sol et de la Concentration de Metaux Lourds dans les Légumes Irrigues avec de l’eau d'étang Extraite dans Jos - Etat du Sud de Plateau

Résumé

L’irrigation des plantes avec de l’eau de l’étang en étain affecte les métaux lourds dans le sol et les légumes et pourrait provoquer des conséquences délétères majeures sur la sécurité alimentaire et la santé humaine. Les métaux lourds dans le sol et les légumes de Jos – l’État du plateau sud irrigué avec de l’eau de l’étang de mine d’étain ont été estimés et se comparent avec les niveaux de contrôle des études récentes et les limites tolérables recommandées. La conception expérimentale a été établie pour déterminer l’accumulation de 8 métaux lourds dans deux sols agricoles et légumes cultivés et irrigués avec de l’eau d’étagère d’étain de chacun des sites. Les résultats montrent que la texture du sol variait du sable limoneux au sable limoneux, le pH légèrement acide 6.2, EC 11,5 - 13,3 DSM-1, OM 5,60 - 5,90, g / kg CEC 19,0 - 21,2 meq, TN 10,2 g / kg, AP 8,8 g G. / kg, k 0,65 - 0,86 g / kg et na 0,22 - 0. 57 g / kg. La concentration de métaux dans le sol irriguée avec l’eau de l’étang mine variait de PB 78.3 - 94,2, Cu 83.0 - 83,4, CD 4.43 - 4.64, Zn 77.1 - 78,16, CR 26.2 - 16,2, Fe 552 - 567, Mn 16,8 - 60,7 et 125 et 125 - 146 mg / kg. Les métaux lourds étudiés dans les légumes de la ferme A et B présentaient différentes gammes, tomate 0,015 - 1,794 mg / kg, œuf de jardin 0,001 - 1,174 mg / kg, poivre 0,007 - 1,556 mg / kg, chou 0,011 - 1,29 mg / kg, carotte 0,010 - 1,59 mg / kg et épinards 0,010 - 1,18 mg / kg. Dans l’étude, il a été observé que l’eau de la mine d’étain utilisée pour l’irrigation des légumes du sol *augmente les concentrations des métaux Pb, Cr, Cd, AS et Mn à divers degrés au-dessus des normes recommandées qui / FAO, 2010, EU, 2002.*

Mots-clés: irrigation, métaux lourds, étain - mines, légumes

المعلمات الفيزيائية والكيميائية لتركيز التربة والمعادن الثقيلة في الخضروات المروية بمياه البركة المستخرجة من القصدير في جوس - ولاية الهضبة الجنوبية

الملخص

يؤثر ري النباتات بمياه بركة مناجم القصدير على المعادن الثقيلة في التربة والخضروات وقد يتسبب في عواقب وخيمة على سلامة الأغذية وصحة الإنسان. تم تقدير المعادن الثقيلة في التربة والخضروات في ولاية جوس-جنوب هضبة المروية بمياه بركة منجم القصدير ومقارنتها بمستويات التحكم في الدراسات الحديثة والحدود المسموح بها الموصى بها. تم إنشاء التصميم التجريبي لتحديد تراكم 8 معادن ثقيلة في تربة زراعية وخضروات مزروعة ومروية بمياه بركة منجم القصدير من كل موقع. أظهرت النتائج أن قوام التربة تراوح من الرمل الطيني إلى الرمل الطيني ، ودرجة الحموضة 6.2 حمضية قليلاً ، EC 11.5 - 13.3 ديسيمتر -1 ، OM 5.60 - 5.90 جم / كجم ، CEC 19.0 - 21.2 ميكرون ، TN 10.2 جم / كجم ، AP 8.8 جم / كجم ، K 0.65 - 0.86 جم / كجم و Na 0.22 - 0. 57 جم / كجم. تراوحت تركيزات المعادن في التربة المروية بمياه أحواض المناجم من الرصاص 78.3 - 94.2 ، النحاس 83.0 - 83.4 ، الكادميوم 4.43 - 4.64 ، الزنك 77.1 - 78.16 ، 26.2 - 16.2 ، الحديد 552-567 ، المنغنيز 16.8 - 60.7 و 125. - 146 مجم / كجم أظهرت المعادن الثقيلة التي تم فحصها في الخضروات من المزرعة A و B نطاقات مختلفة ، الطماطم 0.015 - 1.794 مجم / كجم ، بيضة الحديقة 0.001 - 1.174 مجم / كجم ، الفلفل 0.007 - 1.556 مجم / كجم ، الكرنب 0.011 - 1.29 مجم / كجم ، الجزر 0.010 - 1.59 مجم / كجم وسبانخ 0.010 - 1.18 مجم / كجم. لوحظ في الدراسة أن مياه مناجم القصدير المستخدمة لري خضروات التربة تزيد من تركيزات المعادن Pb و Cr و Cd و As و Mn بدرجات مختلفة أعلى من المعايير الموصى بها WHO / FAO، 2010، EU، 2002.

الكلمات المفتاحية: الري ، المعادن الثقيلة ، القصدير - التعدين ، الخضار

Introduction

Pollution of the environment with metals, including toxic heavy metals, is a growing problem worldwide. Metals cannot be degraded; therefore, they are continuously being deposited and incorporated in the soil, sediment and water, thus causing metal contamination in water bodies and vegetables. The presence of these metals in the water may have a profound effect on the entire ecosystem. Apart from destabilizing the ecosystem, the accumulation of these toxic metals in the aquatic food web is a threat to public health and thus their potential long-term impact on ecosystem integrity cannot be ignored (Paul *et al*., 2014).

Heavy metals in the soil are derived from natural components or geological sources as well as from human activities or anthropogenic sources. Normally heavy metals in soil are found in several forms. These forms are involved in their movement from soil to plant. The conversion of immobile or non-bioavailable forms of heavy metals to mobile or bioavailable forms is a dynamic phenomenon in the soil and occurs continually and is regulated by physical, chemical and biological processes and interactions between them.

The study area played host to a lot of mining activities by foreign companies in the eighteenth century, which rendered the area derelict with numerous waste dumps and ponds. The impact of the past mining activities on the landscape is very devastating as several tin mined-out pits ranging from 10 m to about 40 m in depth were left with various hazardous effects. These tin mined-out pits which are filled with water (from years of rainfall) are generally referred to as mine ponds (Mafuyai *et al.,* 2020).

Today, hand methods by a single person or a group of people are used for mining near-surface, high-grade deposits in the study area. The area was therefore described as a “disaster area” by the State government because of its devastated landscape as a result of indiscriminate mining activities over the years (Jaiye, 2013). The people of these areas are predominantly farmers and hunters due to the topography of the area. But with the coming of mining activities and the location of mining camps in many areas within the local government, many of the inhabitants are also engaged in these mining activities.

These mining ponds water is used for irrigating farmland with food crops and also serve as a major source of drinking water and for domestic activities. Local farmers use water from the ponds for irrigation purposes to grow vegetables like tomatoes, pepper, cabbage, carrot, spinach, garden egg and many other varieties of crops. With tin mining activities going on in various sites on the Jos Plateau at informal levels, the social and economic impacts within the natural and built environment of Jos Plateau comes readily to mind (Mafuyai *et al*., 2019). This study was aimed at determining the effects of water from tin mining ponds on the concentration of heavy metals in soil and some selected vegetables in the Jos-South Local Government Area.

Materials and methods

Study Area

Jos - South is a Local Government Area in Plateau State with the headquarter located in Bukuru town. The area lies between latitude 9°46'N to 9°50'N and longitude 8°52'E to 8°55'E with a land area of 510 km^2 and a population of 306,716 people in the 2006 national population census. The area played host to a lot of mining activities by foreign companies' such as British Mines Corporation Limited, Bisichi Jenta Limited, Gold and Base Corporation, Exland and Kaduna Prospectors (Jiya and Musa, 2012). The impact of the past mining activities on the landscape is devastating as several tin mined- dumps were left with various hazardous effects that pose serious threat to human and animal lives (Adiukwu and Ogezi, 2000). The people of these areas are predominantly peasant farmers who engage in the cultivation of the vegetables such as tomatoes, pepper, cabbage, carrot, spinach, garden egg and many other varieties of vegetables.

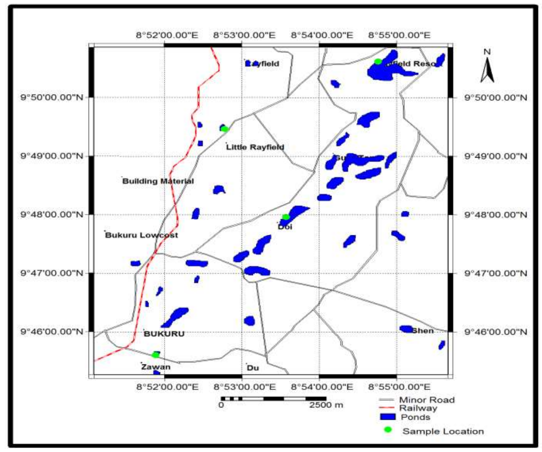

Figure 1 Map of Jos – South Showing Mining Ponds in the Areas

Table 1: Summary of Analytical Procedures used for Physical and chemical Analysis of soil

PARAMETER	PROCEDURE	REFERENCE
Texture	Hygrometer	Gee and Bauder, 1986
pH	pH meter	APHA, 2000
EC	Conductivity meter	Saxane, 1998
CEC	Flame photometry	Reeuwik, 2002
OM	Titrimetric	Walkley and Black, 1934
TN	Titrimetric	APHA, 2010
Na^+	Flame photometry	Black, 1965
K^+	Flame photometry	Black, 1965
AP	Spectrophotometry	APHA, 2011

pH Hydrogen ion concentration, EC Electrical conductivity, CEC Cation Exchange Capacity, OM Organic Matter, TN Total Nitrogen, Na^+ Sodium ion, K^+ Potassium ion, AP Available Phosphorus.

Heavy metals determination

About 5 g of dried and sieved subsoil sample was taken into 100 mL of the conical flask. 20 mL of 1:1 HNO_3 was added to the conical flask and covered with a watch glass. Then the sample was evaporated to 5 to 8 mL on a hot plate. After cooling, 10 mL of $HClO_4$ and 20 mL of metal-free distilled water were added. Then the sample was again evaporated to 10 to 12 mL on the hot plate. After cooling, the sample was filtered through Whatman No. 42 filter paper and the filtrate was transferred to a 100 mL volumetric flask and made up to mark with metal-free distilled water (Hseu *et al.,* 2002). The concentrations of Pb, Cr, Cu, Cd, Zn, Mn, and As were determined by Atomic Absorption Spectrophotometer (Adesuyi *et al.,* 2015). Blanks of the metals were prepared and a calibrated curve plotted.

Calculation

$$\text{Concentration of metal, mg/Kg} = \frac{[(C1-C2) x V x D.F}{D.W}$$

where,

C_1 = concentration of metal in the sample obtained from the calibration curve, mg/L;

C_2 = concentration of metal in the blank obtained from the calibration curve, mg/L;

V = total volume of digested sample, mL;

D.F = dilution factor of digested sample and

D.W = dry weight of the sample, g.

Collection of plant samples and digestion for metal determination

The vegetables; garden egg (*Solanum melongena*), Spinach (*Spinacia oleracea L.*), family: *Amaranthaceae*, Tomato (*Lycopersicon esculatum* L.), family: *Solanaceae,* red pepper (*Capsicum anum*), Carrot (*Daucus carota subsp. Sativus*), family: *Apiaceae*; and cabbage (*Brassica oleracea*) were collected in replicates from two farm irrigated with mined pond water and stored in a labeled polythene sampling bags. The samples were taken to the laboratory and washed with tap water to remove any kind of deposition like soil particles. The edible parts of the vegetables were then dried and ground into powdered forms.

One gram of each milled homogenized sample was weighed using an analytical digital weighing balance into a conical flask. Exactly 5 mL of 60% hydrochloric acid (HCl) and 10 mL of 70% nitric acid (HNO_3) were added into the weighed samples. The sample mixture was digested with moderate heat (50˚C) on hot-plate until white fumes evolved, making it brownish solution. The heat was intensified further for a few minutes to expel most of the hydrochloric acid (HCl). Exactly 50 mL of distilled water was added into the solution and heated for a few minutes, allowed to cool before being filtered through Whatman No. 42 paper into a dispensed transparent plastic container. The filtered sample was then analyzed for the concentrations of lead (Pb), manganese (Mn), chromium (Cr), cadmium (Cd), zinc (Zn), copper (Cu), iron (Fe), using Atomic Absorption Spectrophotometer (AAS) and arsenic (As) by AAS-hydride generation technique. The results were obtained in duplicate and blanks were prepared and the mean values of samples obtained.

Results and Discussions

The mean values along with the standard deviations for the soil parameters (pH, EC, $CaCO_3$ OM, CEC, TN, AP, K, Na) irrigated with tin mine pond water are presented in Table 2.

Table 2: Physicochemical parameters of soil irrigated with tin mining pond water

Parameters	Mean ±SD	
	Farm A	Farm B
pH	6.05 ±0.33	6.20 ±0.33
EC (dSm^{-1})	13.3 ±2.06	11.5 ±2.06
OM ($g\ kg^{-1}$)	5.93 ±1.37	5.60 ±1.37
CEC (meq)	21.2 ±1.09	19.0 ±1.09
TN ($g\ kg^{-1}$)	10.6 ±2.66	10.2 ±2.66
AP ($g\ kg^{-1}$)	8.75 ±1.58	8.79 ±2.28
K ($g\ kg.^{-1}$)	0.65 ±0.07	0.86 ±0.07
Na ($g\ kg.^{-1}$)	0.22 ±0.08	0.57 ±0.08

Electrical conductivity, cation exchange capacity, organic matter, total nitrogen, and available phosphorus in the soil are represented as EC, CEC, OM, TN, AP, K and Na respectively. Values of EC, CEC, OM, and elements are expressed in dSm^{-1}, meq Na 100 g $soil^{-1}$, percentage, $gkg.^{-1}$ respectively

pH of the soils

The mean pH of the soil in farm A and B was 6.1 ±0.2 and 6.2 ±0.33. The result shows that the soil is slightly acidic. The lower pH value of mining water irrigated soil agreed with the finding of Brar *et al.* (2000) and Angin *et al.* (2005). The mining water irrigated soils showed slightly lower pH probably due to the high bioavailability elements in the irrigation water. Soil pH helps in regulating the mobility and complexation of heavy metals and heavy metals are immobile to weakly soluble neutral to the alkaline condition due to complexation with soil organic matter (Marsh and Siccama, 1997; Brun *et al.,* 1998). But the lower the pH value the more metal can be found in the solution and thus more metal is mobilized to translocate heavy metals in the cultivated vegetables (Sherene, 2010).

Electrical conductivity (EC)

The mean electrical conductivity (EC) of the irrigated soil collected from both farms was 13.3±1.3 dSm^{-1} and 11.5 ±2.1 which are far higher than the reported 0.21±0.07, 2.94±2.29 and 3.71±2.11 d Sm^{-1} by Mohamed and Tessema (2013). The elevated EC in the soil collected from the irrigated fields soil may be due to the excess evaporation rate and repeated irrigation with diminishing channel flow which can lead to the salinity of the soil (Wagh *et al.*, 2013).

Cation exchange capacity (CEC)

The mean value of CEC in the soil analyzed from the treated farms shows 21.2±0.48 and 19.0 ±0.7 meq Na 100 g $soil^{-1}$ in farm A and B, respectively. The values of CEC reported in this study were lower compared with the 28.07±11.2, 59.06±13.1 and 34.11±4.8 cmol kg^{-1} and high compared to that reported 12.98 by (Mohamed and Tessema, 2013). So, it is possible that a large part of exchangeable bases in the soil must have been existed as a water-soluble form rather than an exchangeable form adsorbed at cation exchange sites Amos *et al.* (2014). The causes of increased CEC in the soil irrigated with tin mine pond water may be due to the addition of clay from the mining activities.

Organic matter (OM)

The mean value obtained in the study sites are 5.93±1.5 mg/kg and 5.60±0.9 mg/kg. There was little variation observed in both farms although the values are quite higher in the soils collected from both sites. The OM reported in this study is much higher compared to 0.48±0.10, 0.86±0.08 and 0.52 ±0.014 by Mahammed and Tessema (2013). The reason may be the application of mining wastewater, containing some elements that contributed organic matter to the soil. Angin *et al.* (2005) highlighted that the organic matter level of the wastewater-irrigated soils was higher than that of the non-wastewater irrigated soils. Soil organic matter has proven to be the most important soil component controlling the sorption and desorption of metals (Maldonado *et al.,* 2008) and plays a crucial role in the mobility and subsequent translocation of soil heavy metals through not only providing sorption site for metals directly, it will also combine with soil minerals and increases the sorption sites.

Total nitrogen

Nitrogen is a virtually important plant nutrient that normally contains 1-5% weight of this nutrient. Ammonium (NH_4^+) and nitrate (NO_3^-) are considered plant available nitrogen in the soil as they are absorbed by plant. The plant available nitrogen content in the tin mining pond water irrigated soil shows a mean concentration 10.6 ±3.1 and 10.2 ±2.7 g/kg in farm A and B, respectively. Monnett *et al.* (1996); Fuentes *et al.* (2002) reported that total soil nitrogen increased under the influence of urban wastewater or wastewater sludge irrigation; and an increase in potassium and phosphorus in the soil as a result of waste water application.

Available phosphorus

Plant available phosphorus amongst others different phosphorus HPO_4^{2-} and $H_2PO_4^-$ are considered as plant-available phosphorus due to their absorption by roots. Absorbed phosphorus is distributed throughout the plant body and it took part in multiple functions (Gupta *et al.*, 2010).

The mean available phosphorus content in the irrigated soils in both farms A and B is 8.75 ±1.7 g/kg and 8.79 ±2.5 g/kg, respectively. The value is lower in both sites, this might be due to the lack of total phosphate content in the mining pond water used in irrigation. Angin *et al.* (2005) showed that the available phosphorus levels of wastewater irrigated soils are high compared to the non-wastewater irrigated.

Higher levels of P ranging from 68.2±0.89 to 84.2±1.02 g/kg have been reported by Mohammed and Tessema (2013) as compared to the lower values in this study. This could be attributed to the absence of high amount of organic matter in the soil and plants decomposition (Ideriah *et al*., 2006). The high concentration of phosphorous contributes to the good growth of plants, as available P values of more than 10 g/kg are considered suitable for crop production.

Available potassium

Potassium is absorbed as K^+ ion by roots. It is present in plants from 1-4 % and its function appears to be primarily catalytic. The mean available potassium content in the soil irrigated with tin mine pond water in the two farms 0.65 ±0.1 and 0.86 ±0.1 g/kg in farms A and B, respectively. From the results it is clear that practically irrigated water is not the contributor of the potassium because the quantity of potassium in the irrigation soil is very less. Wastewater irrigation provides nitrogen (N), phosphorus (P) and potassium (K) to the soils (Siebe, 1998). Kiziloglu *et al.* (2008) also reported an increase of N, P, K exchange able Na, K, Ca, Mg available phosphorus and microelements after irrigation with wastewater thus the exploration of tin involves breaking of the soil surface by dragline or human effort.

Sodium

The mean concentrations of the sodium recorded in both farms were 0.22 ±0.03 and 0.38 ±0.06 g/kg in A and B, respectively. The low concentration of Na in both farms may be unconnected with the geology of the soil.

Heavy metals in tin mining Pond Waters

Lead (Pb): Lead concentration in the mining pond water, used in irrigation of agricultural fields from pond A was 1.62±0.1 and pond B 1.58±0.3 mg/L. Higher lead concentration in the tin mining pond water agreed with the finding of Mahmood (2016); Chopra and Pathak (2012); Singh *et al.* (2012). ***Copper (Cu):*** The mean of Cu in tin mining pond water in the three studied areas in in farm A and B 0.43±0.01 mg/L and 0.16±0.03 mg/L, respectively. The concentration of Cu in tin mining pond water in both ponds exceeds the recommended limits prescribed by FAO/WHO (2007). The higher concentration of Cu in the tin mining pond water as compared with literatures agrees with the findings of other researchers viz., Tukura *et al.* (2016); Mahmood and Malik (2014); Chopra and Pathak (2012) and Singh *et al.* (2012).

Cadmium (Cd): The mean of Cd obtained from the three study areas in dry season is 1.028±0.21 mg/L and 0.199±0.012 mg/L in pond A and B, respectively. The highest concentration of Cd was found in pond A. In both the tin mining pond water studied the value were comparatively higher than 0.07±0.02 mg/L reported by Chopra and Pathak, (2012). and the values agrees with the findings of 0.226 mg/L for Boamponisem (2012). The high concentration of cadmium is said to be attributed to the large-scale mining activity that took place and still going on within the vicinity in a small scale. The two tin mining pond water used the irrigation crossed safe standards of WHO/FAO (2007) and USEPA (2010) prescribed limits of 0.01 and 0.005 mg/L, respectively.

Zinc (Zn): The Zn concentration in mining pond water A and B are 0.75±0.31 and 0.74±0.08 mg/L, respectively. The mean value of Zn in both ponds were quite higher but, comparing with the prescribed standard of irrigation value it is found that Zn concentration in the water irrespective of pond were within the limit of prescribed FAO/WHO (2007). The high concentrations of zinc measured in this study could be due to weathering of geological materials and possibly small-scale mining still going on in the area in addition to runoffs from farms could also affect the concentration since some agrochemicals contain zinc were applied closed to sample areas

Chromiun (Cr): Chromium concentration in the tin mining pond wastewater of both ponds were 0.35±0.3mg/L and 0.35±0.07 mg/L in pond A and B, respectively. The concentration of Cr in the tin mining pond water in both ponds corroborated with the findings of Henry *et al*. (2018) reported 0.38 mg/L in ex-mining pond in Plateau State. The tin mining pond water showed higher Cr concentration compared to the prescribed standard limit by WHO/FAO (2007) and USEPA (2010), respectively.

Iron (Fe): Iron was the most abundant metal detected in all the water samples from all ponds. The mean concentration of iron ranged from 1.104 – 6.392 mg/L and were within the FAO permissible limit of 5.00 mg/L for irrigation water (Ayers and Westcot, 1994). The findings indicated a high occurrence of iron at the study ponds were 4.77±0.5 mg/L and 4.69±0.3mg/L in farm A and B, the values reported in this work for Fe are within the permissible FAO but however, lower than 14.08 mg/L reported by Boamponisem *et al*. (2012) and 16.4 mg/L by Brar *et al.* (2000).

The presence of iron in the water samples could be attributed to natural geological weathering. However, the higher levels recorded in the ponds could be due to excavation and processing of ore by mine operators exposed the geological material to the agents of weathering thereby increasing the rate of minerals dissolution into water bodies Abdul-Razak *et al.* (2009).

Manganese (Mn): The concentration of Mn in farm A and B were obtained, 1.24±0.5 mg/L, and 1.07±0.5 mg/L respectively. In both of the tin mining pond waters Mn concentration was higher than the prescribed standards. The high levels of Mn observed in the water can be attributed to anthropogenic activities, particularly large-scale mining and the activities of excavator machines working on the mines sites. These has influence on the flux of metals from geological materials to the hydrosphere through dissolution of minerals (Akabzaa *et al.,* 2009). Manganese concentration in mining pond water used for irrigation is agrees with the findings of Bharose *et al.* (2013); Singh *et al.* (2012).

Arsenic (As): The mean of arsenic tin mining pond waters in the studied ponds A and B were 0.95±0.2 mg/L and 0.94±0.4 mg/L. The concentration is higher compared with 0.04 mg/L reported by Brar *et al.* (2000) in sewage water used for irrigation in Northwest India. Arsenic in water is mostly present as As^{5+}), but in anaerobic conditions, it is likely present as As^{3+} WHO, (2010). Arsenic in drinking water is a global threat to health (United Nations International Children's Emergency Fund UNICEF (2008); World Health Organization WHO (2010). It is considered by some researchers to have more serious health repercussions than any other environmental contaminant. The concentration reported in this work is very high compared to guideline value of 0.01 mg/L given to it by the World Health Organization.

Table 3. Textural of Soil irrigated with mining pond water

Samples	Farm A soil properties				Farm B soil properties			
	Clay %	Sand %	Silt %	Soil type	Clay %	Sand %	Silt %	Soil type
C_1	22	48	30	Sandy Loamy	19	54	37	Loamy Sandy
C_2	18	51	31	Sandy Loamy	24	49	27	Sandy Loamy
C_3	21	50	29	Sandy Loamy	22	47	31	SandyLoamy
C_4	20	49	31	Loamy Sandy	23	52	25	SandyLoamy

Texture

Soil texture refers to the relative percentage of sand, silt and clay in a soil. Texture is an important soil characteristic that determines cultivation and irrigation. The texture of soil in farm A and B was similar made of loamy sand and sandy loamy soils with clay fractions. The clay fraction of the soils is very active and is important adsorption media for heavy metals in soils as well as plays an important role in the mobility of metals in soil (Sherene, 2010). The soil samples, collected from the mining pond water irrigated plots represented sandy loam to loam clay texture throughout the study. From the studied soil texture, it reflects that the soil contains a low to the intermediate quantity of clay and which might not be responsible to retain much more heavy metals.

All sites have a soil color of light brown when moist. This physical property has a significant influence on the infiltrate rate and hydraulic conductivity of the soil as well as the retention and movement of irrigation water around the root zone (FAO, 2000). Generally, the results of the particle size analysis indicate that most of the soils are heavily textured. Moreover, the mass of surface soil layers has a weakly developed platy structure while the subsurface soil layers have developed platy structure with good porosity. These properties have an impact on the movement of air and water within the soil (Brady and Weil, 2002). Medium infiltration rate was observed in all the sampled sites. However, the infiltration rate at the beginning of the test was lower when compared with the theoretical rate that is attributed to the platy structure of the soil, that is, it could impede the downward movement of water. This with the findings of Jiya and Musa (2012). As well, the availability of deep soil depths in the study site implies that soil depth is not a limiting factor to produce most field crops.

Heavy Metals Concentration in Soil irrigated with Tin Mining Pond Water

The mean concentrations of the heavy metals with their various standard deviations in soil irrigated with tin mining pond water are presented in Figures 2, 3 and 4. The mean of Pb in the soil samples collected from both farms fields showed little higher value in the soil irrigated with tin mining pond water than in control soil. The mean value obtained was 94.2±13.3 and 79.3±3.8 mg/kg for farm A and B, respectively. The result shows that the concentration of Pb in both two farms is slightly different and higher than the values obtained in the control farm

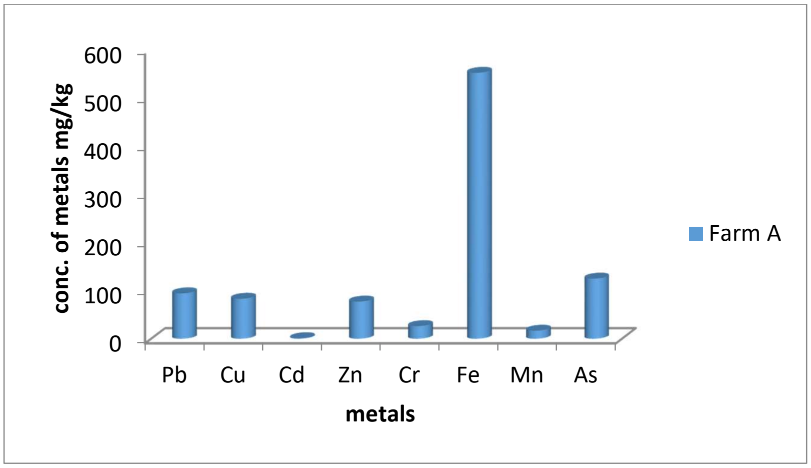

Figure 2. Concentration of heavy metals in soil irrigated with mine pond water

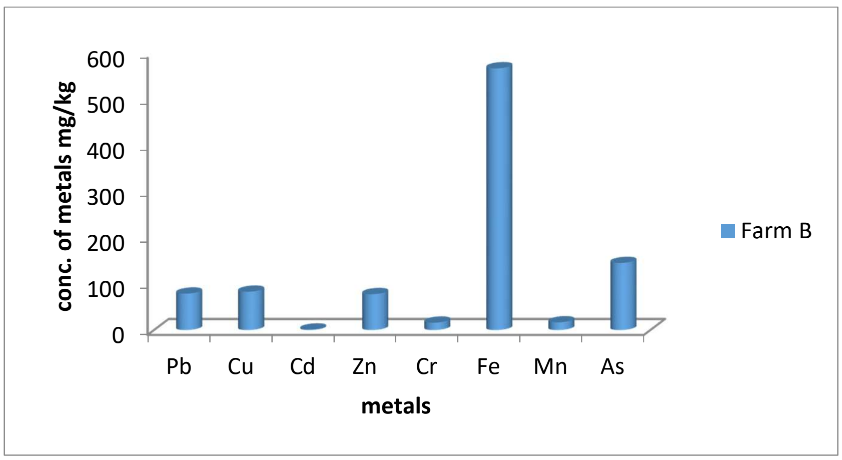

Figure 3. Concentration of heavy metals in soil irrigated with mine pond water

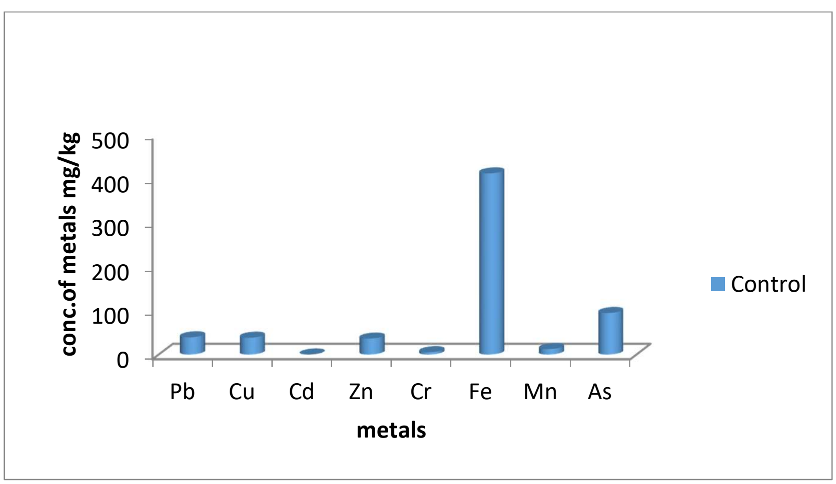

Figure 4. Concentration of heavy metals in control soil

The concentration of lead in farm A soil irrigated with mine pond water is higher than that of farm B in the study areas. All the reported values are within the prescribed safe limit of irrigation soil FAO/WHO, (2008) standard limits. The value of Pb obtained is comparable with that reported by Daniel *et al.* (2014) in Kassa Ropp Barkin-Ladi. Similar work done by Mahmood, (2016) revealed Pb concentration in soil to range from 1 – 58 mg/kg. Ratul *et al.* (2018) reported 28.13 mg/kg in agricultural soil irrigated with contaminated river water lower than the concentration reported in this study. The enrichment in Pb by the mining pond water irrigated soils as compared to the control soil collaborated with the findings of 15.4 ±6.6 mg/kg and 9.31 ±2.2 mg/kg for Mahmood and Malik (2014); Lente *et al.* (2012).

The mean value of Cu in mining pond water irrigated soil from farm A and B is 83.0 ±21 and 83.4 ±6.0 mg/kg, respectively. The values compared to control soil 38.3 ±2.6 mg/kg) shows that there is an accumulation of Cu in the soil which might have been because of anthropogenic and industrial processes. The Cu concentration of the irrigated soils is within the safe limit for cultivation. The study also showed a significant difference ($p < 0.05$) in the Cu content of control and treated soils collected in both seasons. This result is similar to the findings of 42.0 – 111.6 mg/kg of Kabir *et al.* (2017) which recorded extremely high concentrations of copper at industrial sites. Ratul *et al.* (2018) also reported higher concentrations of Cu 69.01 mg/kg in agricultural soil irrigated with contaminated river water.

The mean concentration of Cd in the mining pond water-treated soil A and B is 1.14 ±0.6 and 1.201±0.6 mg /kg which is double as compared with the Cd content of control soil 0.145 ±0.01mg kg/kg analyzed during the period. The concentration obtained in this work for soil treated with tin mining pond water agrees with the 0.965 mg/kg reported by Ratul *et al.* (2018) in agricultural soil irrigated with contaminated river water. Comparing with the safe limit of Cd in the soil it is found that treated soils in both farms are within the prescribed standards of 3 – 6 mg/kg set by Indian Awashti (2000) and USEPA (2010). The relative cadmium concentration in soil may be attributed to the applications of fertilizers and other farming practices including the use of pesticides. Generally, the high concentrations of metals in this area could also be as a result of the tin mine activities and metals availability in the earth's crust.

In this study Cd concentration in both irrigated soils are lower compared to the literature values of 15.4±6.6 mg/kg, 3.54±0.6 mg/kg and 9.91±1.1 mg/kg reported by Mahmood and Malik, (2014); Daniel *et al.* (2014) and Gupta *et al*. (2016), respectively.

The mean concentration of Zn in the mining pond water-treated soil was 77.14 ±6.3 and 78.16 ±2.7 mg/kg for farm A and B, respectively. The result obtained is higher than the control soil with mean concentration of 36.2 mg/kg. From the value of Zn content in the tin mining pond water used for irrigation, it is clear that the water has the potential for the development of Zn enrichment. Both the soil samples analyzed during the study have been found to be enriched with Zn more than the control soil. The Zn content in both studied soil is within the safe limit of 200 mg/kg prescribed by USEPA (2010). The Zn concentration in the wastewater irrigated soil reported in this study is in agreement with wastewater-irrigated soil concentrations of 50.8 ±29 mg/kg published by Mahmood and Malik, (2014) and reported concentration of 45.7 mg/kg by Ratul *et al.* (2018) in agricultural soil irrigated with contaminated river water; but however, higher compared to the result of 3.9 ±0.1 and 6.03±1.7 mg/kg reported Tukura *et al.* (2016) and Lente *et al*. (2012), respectively.

The soil samples collected from fam A and B exhibit the mean Cr content of 26.15 ±4.6 mg/kg and 16.19 ±1.7 mg/kg respectively, when irrigated with tin mining pond water. It was observed that Cr in both farms doubled more than two times higher than in control soil 5.34 ± 2.3mg/kg. The result reported in this study agrees with the 22.9 mg/kg reported by Ghosh *et al*. (2012) and 20.01±11.3 mg/kg by Mahmood and Malik (2014). The concentration obtained even though high, is lower than the value of 54.2 mg/kg reported by Daniel *et al.* (2014) in Kassa Ropp for similar tin mining soil and 69.75mg/Kg reported by Ratul *et al.* (2018) in agricultural soil irrigated with contaminated river water. However, the low value in this study may be attributed to the leaching of metals beneath the soil. The Cr concentration in the soil of the two farms is within the 150 mg/kg safe limit of the EU (2002) standard.

The mean concentration value of the control soil was 412 ± 8.1 mg/kg. The soil sample irrigated with tin mine pond water was 552 ± 44 mg/kg and 567 ±5.1 mg/kg for farm A and B, respectively. Higher concentrations of Fe was observed in the soil irrigated with tin mine ponds water, the washing of mining piled dumps by runoff water during rainfalls may also be a contributing factor Mafuyai *et al*, (2019). The results show that iron (Fe) is the most abundant essential metal in both farm soils. **The** variations in the absorption of Fe from the soil by the plant's tissues are evident in the low Fe contents in the vegetable samples. The high concentrations of Fe in the soil samples may suggest a very rich anthropogenic source of Fe, which allows the percolation of Fe to the soil depths rather than the surfaces. Boamponisem *et al.* (2012) reported 14.1 mg/kg lower values of Fe as compared to this work.

The soil irrigated with tin mine pond water showed significantly similar average Mn content of 16.68 ±1.9 mg/kg and 16.19 ±1.3 mg /kg in farm A and B, respectively compared with control soil concentration of 6.64 mg /kg. This may be attributed to accumulation washing from different places such as roads, and ashes from burned vegetation washed down by rainfall. However, the increased in Mn content in the tin mine pond water irrigated soils shows lower concentration compared with ground water irrigated soils with 39.0±22.6 mg/kg findings of Mahmood and Malik (2014) and Gupta *et al.* **(**2010).

The mean concentration of As in mining pond water irrigated soil had concentration of 124 ±56 mg/kg in farm A and 145 ±22 mg/kg in B, respectively. The highest concentration was recorded in Farm B with the lowest being in control soil 94.3 ±22 mg/kg showing that there is an accumulation of As in the soil as a result of industrial wastes and pesticide applications which might increase concentrations. Thus, the As level in the tin mine pond water irrigated soils is within the safe limit for cultivation. Naturally elevated levels of arsenic in soils may be associated with geological substrata such as sulfide ores therefore, anthropogenically contaminated soils can have several concentrations of arsenic Sanok *et al.* (1995). The soil of agricultural land treated with arsenical pesticides may retain substantial amounts of arsenic. Mean total arsenic concentrations of 50 – 60 mg/kg have been recorded for agricultural soils treated with arsenical pesticides (Dorcas *et al.,* 2014).

Heavy Metals Accumulation in Cultivated Vegetables

The mean results of heavy metals determined in vegetables irrigated with tin mined water pond are as shown in table 4 and 5.

Tomato: The result shows that Pb concentration in tomato farm A and B in the study areas is in the range of 0.39±0.1 - 0.40±0.01 mg/kg, respectively. The highest value was observed in farm B tomato; this is evident as there are still local miners operating in the area. The values obtained are similar to the value 0.26 – 0.70 mg/ kg by Mahmood and Malik (2014); and 1.15±0.29 mg/kg reported values by Duressa and Leta (2015) in soil and some vegetables which showed concentrations above the maximum permissible limit and standard value. Nassar *et al*. (2018) also observed high levels of Pb (2.40±0.99) mg/kg and Cd (0.25±0.11) mg/kg in wastewater - irrigated tomatoes in Egypt. Al-Jaboobi *et al.* (2014) reported higher concentration of 10. 75 mg/kg in wastewater-irrigated tomatoes.

Table 4: Mean Concentration ±SD mg/kg of heavy metals in vegetables irrigated with tin mining pond water in farm A

Metal	Vegetables					
	Tomato	Garden Egg	Pepper	Cabbage	Carrot	Spinach
Pb	0.392±0.07	0.316±0.014	0.177±0.01	0.271±0.05	0.545±0.03	0.376±0.03
Cu	0.077±0.01	0.085±003	0.440±0.12	0.073±0.01	0.155±0.02	0.748±0.02
Cd	0.019±0.01	0.006±0.01	0.006±0.01	0.011±0.01	0.013±0.1	0.005±0.00
Zn	0.619±0.17	0.349±0.03	0.415±0.02	0.264±0.05	0.915±0.06	0.555±0.03
Cr	0.131±0.01	0.114±0.01	0.132±0.03	0.089±0.03	0.158±0.04	0.115±0.00
Fe	1.742±0.22	1.062±0.0y	1.556±0.07	0.330±0.01	1.585±0.26	1.181±0.03
Mn	0.184±0.01	0.186±0.01	0.253±0.03	0.164±0.02	0.682±0.04	0.162±0.01
As	0.215±0.03	0.056±0.01	0.032±0.002	0.043±0.04	0.245±0.05	0.050±0.01

Table 5: Mean Concentration ±SD mg/kg of heavy metals in vegetables irrigated with tin mining pond water in farm B

Metal	Vegetables					
	Tomato	Garden Egg	Pepper	Cabbage	Carrot	Spinach
Pb	0.491±0.11	0.279±0.02	0.307±0.26	0.164±0.03	0.465±0.02	0.455±0.04
Cu	0.071±0.01	0.832±0.06	0.065±0.00	0.065±0.01	0.090±0.01	0.062±0.01
Cd	0.009±0.01	0.002±0.01	0.006±0.01	0.005±0.00	0.022±0.01	0.014±0.01
Zn	0.376±0.04	0.450±0.03	0.395±0.02	0.184±0.02	0.913±0.06	0.448±0.03
Cr	0.154±0.03	0.131±0.01	0.106±0.01	0.108±0.01	0.143±0.02	0.147±0.03
Fe	1.55±0.21	1.33±0.18	1.49±0.03	1.435±0.07	1.65±0.14	1.55±0.21
Mn	0.454±0.39	0.332±0.31	0.177±0.01	0.166±0.01	0.791±0.15	0.115±0.01
As	0.076±0.01	0.027±0.01	0.033±0.02	0.028±0.01	0.466±0.39	0.046±0.00

The mean concentration of Arsenic was 0.22 mg/kg in tomatoes farm A and 0.074mg/Kg in farm B. This concentration is high compared to 0.06±0.02 mg/kg by Bambara *et al.* (2015) and lowers than the 0.62±0.19 mg/kg findings by Duressa and Leta (2015). The high value of Arsenic might be due to the discharge of used oils from the drag-line operating in the tin mining ond or leather/tannin Company which discharges its influents close to the pond. The concentration of As in this study is above the recommended standard guidelines by WHO/FAO, (2007).

The mean of Cr was also high in the study areas, 0.13±0.01 and 0.16±0.01mg/kg in in the tomato farm A and B, respectively. The high value of Cr obtained in this study is lower compared to 0.66 mg/kg reported by Orish *et al.* (2018) and 2.97 mg/kg by Yadav *et al.* (2013) in a similar work. The values obtained are higher than the recommended standard.

Mn has a concentration of 0.183 mg/kg in the tomato collected from both two farms, a value higher than the recommended standard. This may be attributed to the accumulation of washings from different places such as roads and ashes from burned vegetation washed down by rainfall.

However, Cd was high in both tomatoes collected from farms A and B, this might have been due to washing by runoff water from the immediate vicinity since several anthropogenic processes took place and are still occurring on small scale by illegal miners. This is agreed with the 0.12 mg/L reported by Saglam (2013) in the study of vegetables in Southern Turkey. The high concentrations of some of these metals in the areas could be a result of the closeness of the mining ponds to major traffic highways. The order of metal concentration in tomatoes collected from farm A and B in this work is; Fe > Zn > Pb > As > Mn > Cr > Cu > Cd and Fe > Zn > Pb > Mn > Cr > As > Cu > Cd, respectively. Heavy metal accumulation in tomato due to long-term wastewater irrigation was also highlighted by Henry *et al*. (2018).

Garden egg: The mean concentrations of each heavy metal for vegetables in the two sites shows that Pb (0.4), Cr (0.131), As (0.06) and Mn (0.83) mg/Kg were higher than the standard permissible limit FAO/WHO (2011), while the concentration Fe and Cd are lower compared to other metals standards. The order of heavy metals accumulation in the garden egg from farm A and B was Fe > Zn > Pb > Mn > Cr > Cu > As > Cd and Fe > Mn > Zn > Pb > Cr > Cu > As > Cd, respectively. The results obtained in this study were similar to the reported studies by Aljaboobi *et al*. (2014); Shibao *et al.* (2016). Auta *et al.* (2011) also reported high levels of Zn (3.91) and Cd (1.56) mg/Kg in wastewater-irrigated garden egg in Kaduna, Nigeria. Tukura *et al*. (2016) reported high levels of Zn (1.60) and Pb (0.36) mg/Kg.

Pepper: The mean concentration of Pb in both peppers collected from farms A and B was 0.176 mg/ Kg and 0.145 mg/kg, respectively. The concentration of Cd was slightly lower in all the study areas 0.007 and 0.009 mg/kg in pepper farm A and B while that of Mn was 0.250 mg/Kg in both pepper studied. The order of concentration of the heavy metals in the pepper was Fe > Cu > Zn > Mn > Pb > Cr > As > Cd and Fe > Zn > Mn > Pb > Cr > Cu > As > Cd, respectively. The concentrations of Mn, Cr, Pb and Cd in pepper in the studied areas have crossed the prescribed safe value of WHO/FAO (2011) and EU standard (2002), respectively. The high concentration of metals in pepper might be attributed to high level of pesticides and fertilizer on farmland for better yield of crops. Wastewater induced heavy metal accumulation in vegetables is also reported by Adotey *et al.* (2009) Mn (19.1±1.7) mg/kg accumulation in vegetables grown on farmlands irrigated with treated sewage water in Ghana. Duressa and Leta (2015) reported 1.15±0.29 mg/kg accumulation of Cd in pepper. Dorcas *et al*. (2016); Jolly *et al.* (2013); Abdu *et al*. (2011) and Sinha *et al*. (2006) also reported high concentration of heavy metals in vegetables irrigated with wastewater from mines and industrial discharges to soils.

Cabbage: The mean concentration of Pb 0.27±0.05, and Cr 0.09±0.04 mg/kg was found in cabbage is high from both farms with other metals in lower concentrations than the value 3.98±4.9mg/kg reported by Boamponsem *et al.* (2012). Cd was also slightly high in the dry season with a value of 0.011 mg/kg at both sites but lower than 0.22±0.2 mg/kg reported by Benti (2014) and 6.25±1.2 mg/kg Kumar *et al*. (2018). Similar studies conducted by Henry *et al*. (2018); Nassar *et al.* (2018), show the same trend of metal behavior in vegetables. The order of concentration of the heavy metals in cabbage collected from farms A and B Fe > Zn > Pb > Mn > Cu > As > Cr > Cd and Fe > Pb > Zn > Mn > Cr > Cu > As > Cd, respectively. It was therefore, noted that Pb and Cr are high in cabbage crossing the standard permissible limits FAO/WHO (1985). The high levels of these metals in this vegetable might be a result of the use of pesticides and her

Carrot: The results of the study shows that the concentrations of the metals are higher in the entire field of carrot except for metals Cu, Zn, and Fe have not crossed the safe limit of FAO/WHO, (2008) standards and EU, (2002) standard. Carrots from all the farms were not safe for human consumption as their concentrations were above the maximum permissible limit, 0.30 mg/kg. The mean concentrations of all the heavy metals in carrot ranged from 0.01 –1.59 mg/kg with Mn, Pb, As and Cr, having the high concentration mean in farm A: 0.68 mg/Kg, 0.55 mg/kg, 0.25mg/kg and 0.16 mg/kg respectively. Francis, (2014) also reported 1.23±0.2 mg/kg Pb in carrot. The studied metals are in descending order of Fe > Zn > Mn > Pb > As > Cr > Cu >Cd in farm A and B, Fe > Zn > Pb > Mn > Cu > Cr > As > Cd. Mahmood and Malik, 2014; Tukura *et al*. (2016) and Roy and Gupta, (2016), reported high concentrations of heavy metals in carrot due to irrigation with wastewater, respectively. Heavy metals accumulation in wastewater-irrigated carrot also is studied by Arora *et al*. (2008) and Sadhu *et al*. (2015).

Spinach: The concentrations of all the metals studied in all sites A and B were found to have high metals in spinach but others show lower values. Pb, Mn, As and Cr concentrations ranged from 0.03 – 0.40 mg/Kg with the highest value obtained in farm B, as 0.40, 0.16, 0.05 and 0.13 mg/Kg, respectively. Comparing the concentration heavy studied in spinach, with other literatures, it found that the values obtained for Pb are lower than the findings of 2.9±1.2 mg/Kg by Mahmood and Malik, (2014); 1.50±0.1 mg/kg Abdul-Razak (2009); 15.1 mg/kg by Sadhu *et al.,* (2015); 2.78 mg/kg by Gupta *et al.,* (2013). Kumar *et al.* (2017) reported 3.31mg/kg concentration of Cr in spinach and Abdul *et al*. (2015) reported Cd and Mn 0.34±0.1 and 17.0±3.2 mg/kg in spinach respectively in agricultural soil irrigated with contaminated river water, which is far higher than the value reported in this work.

Compared with the prescribed standards it is found that Pb, As, Mn and Cr content in spinach have crossed the safe limit of WHO/FAO (2010) and EU (2002). However, the major sources of vegetable contamination with heavy metals might be due to the tin mine pond water used to irrigate the spinach, wearing of machine parts of the equipment used in tin exploration, vehicular exhaust and agrochemicals Muchaweti *et al*. (2006). Wastewater-induced heavy metals enrichment in spinach was studied by Yadav *et al.* (2013). The variations in heavy metal concentrations in vegetables of the same site may be ascribed to the differences in their morphology and physiology for heavy metal uptake, exclusion, accumulation and retention (Kumar *et al.,* 2009).

Conclusion

The use of tin mining pond water for irrigation in this part of the country is a common practice. This practice is driven by factors like easy availability and scarcity of irrigation water during the dry season. In this study, tin mining pond waters was used in the irrigation of six different vegetable and the concentration of heavy metals Pb, Cr, Cu, Cd, Zn, As, Fe and Mn evaluated and compared with the prescribed standards of FAO/WHO, USEPA, EU. The soil collected from the irrigated fields shows the improvement of soil heavy metals compared with soil collected from farm not irrigated with tin mine pond water. Among all studied metals Cd, Cr, Pb, As and Mn were found higher than prescribed standards in some of the vegetables. The low concentrations of Fe, Cu, and Zn in the vegetable samples relative to their abundant availability in the soils can be attributed to; the low absorption of these metals by the tissues of the vegetable samples, possibly leaching as a result of the soil surface and runoff during rainfall.

The tin mining pond water does not pose a significant effect on the soil but, Pb, Cd As Mn and Cr in the soil compared to other metals studied considering their accumulation in some vegetables call for regulatory mechanism. Therefore, regular monitoring of effluents and soils, is essential to prevent excessive build-up of the toxic heavy metals in soil which may eventually be transferred to planted crops and vegetables in the area.

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