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Heavy Metals in Soil and Vegetables Irrigated with Ex- Tin Mining Ponds Water in Barkin - Ladi Local Government Area Plateau State, Nigeria

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Abstract

Tin mining pond water irrigated fields can cause potential contamination with heavy metals to soil and vegetables, thus pose a threat to human beings. The current study was designed to investigate the contamination of the soil with toxic heavy metals and their accumulation in edible vegetable crops. The heavy metals Pb, Cu, Cd, Zn, Cr, Fe, Mn and As were analyzed for their bioaccumulation factors to provide baseline data regarding environmental safety and the suitability of tin mining pond water for irrigation in the future. The contamination factor (CF) of these metals in the soil were calculated and indicated levels of metal contamination in the order of Cd > Zn > Pb > Cr > Cu > As > Fe > Mn. The concentrations of Pb, Cd, Cr, As, and Mn in the edible vegetables were above the safe limit prescribe by FAO/WHO, 2007 and EU, 2002 in all studied vegetables. The results indicated a potential pathway of human exposure to slow poisoning by heavy metals due to the utilization of vegetables grown on heavy metal contaminated soil that was irrigated with tin mining pond water sources. Amongst the studied vegetables, As and Cr were observed to exceeds tolerable limit. The irrigation source was identified as the source of the soil pollution in this study. Thus, their consumption might pose substantial health risk to consumers and therefore need for proper remediation to reduce health risk and the extent of heavy metals contamination.

Keywords: Heavy metals, Contamination, Vegetables, Tin - Mining.

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Contents

Contribution of this paper to the literature
This study contributes to existing literature by providing a baseline research on heavy metals in ex-mining pond water accumulation in vegetables and the need for quotient.

1. Introduction

Mining of solid minerals has been identified as a major entry point of heavy metals into the environment consequently polluting various components of the environmental media [1]. Mining, which involves the extraction of naturally occurring minerals from the earth's crust, is considered the world's second oldest and most important industry after agriculture [2]. In the process of mining a particular metal the entire soil mass is excavated, laid bare and expose to the environmental agencies of weathering, degradation and transportation, this result in soil erosion and extensive contamination of the surrounding areas. The abandoned ponds and dumps tailing scattered still impact the environment by contaminating vegetables as well as pollution of underground water by discharged leachate [3].

Heavy metals are considered as one among the most important environmental concerns because of their toxicity and accumulation in body [4],[5],[6]. Heavy metals are those metals which have a specific density of more than 5 g/cm3 and harmfully affect the living organisms as well as environment and living organisms [7]. These metals are essential to maintain the normal body physiology and functioning when present in very low concentrations. However, they become lethal when certain threshold levels exceed. Many studies have been conducted throughout the world in relation to plants and soil pollution with heavy metals through irrigation by urban and industrial effluents [8]. Vegetables are important components of a healthy and perfect diet of human beings [9].

In a developing like country like Nigeria, the fight against poverty, hunger, malnutrition and undernourishment continues to be a basic goal of development and a variety of strategies are being applied based on micronutrient rich food like vegetables considered essential. These Vegetables are the fresh and edible portions of herbaceous plants. They are very popular in Nigeria, though, its production is low in rainy season compared to dry season due to differences in environmental conditions, non-availability of high yielding varieties and cultural practices in the crop production [10]. They are important class of food substances highly beneficial for the maintenance of health and prevention of diseases [11].

The inclusion of vegetables in human diets has been identified as a major means of promoting balanced diets across populations of various income brackets [12]. This is because green vegetables have been recognized as one of the richest natural sources of essential minerals, protein and vitamins. In addition to being cheap sources of macro and micronutrients, vegetables could also be efficiently produced with limited resources. The regular consumption of vegetables, specifically the dark green leafy vegetables is highly recommended because of their potential in reducing the risks of chronic diseases [13],[14].

Mining generally enriched heavy metals in soil leading to elevated levels in both plants and water samples [15]. Sometimes the metals are very well preserved for hundreds of years and can remain a potential hazard for the environment. Heavy metals are currently of environmental concern due to their bioaccumulation in soil and vegetables [16]. The soil, water and vegetable resulting from mining operations contain potentially carcinogenic levels of heavy metals and these elements could be related to the high prevalence of upper gastrointestinal cancer rates in the in the country [13]. The determination of heavy metal distribution in plants and environmental media is one of the most accurate criteria related to environmental pollution [17]. The accumulation of heavy metals in agricultural soils is of increasing concern because of food safety, potential health risks, and its detrimental effects on soil ecosystems [18],[19]. The accumulation of heavy metals in cultivated plants due to environmental media, fertilizers, and pesticides have a negative effect on plant growth and human health. The concentrations in plants can affect humans directly either through ingestion or through the food web by ingestion of crops or animals or indirectly-damaging environmental health [20]. The environmental exposure to heavy metals is a well-known risk factor for cancer [13]. Some metal ions like cadmium, lead and, chromium have toxic effects on biochemical reactions in our body. Heavy metals can be harmful due to their potential accumulation in different tissues of humans. Even in low concentrations, heavy metals have detrimental health effects, because they are non-biodegradable and persistent in nature [21],[17]. The health risks of heavy metals through consumption of vegetables from these mining soils are of great concern in the study area.

Irrigation has contributed significantly to poverty alleviation, food security, and improving the quality of life for rural populations. However, the sustainability of irrigated agriculture is being questioned, both economically and environmentally. The increased dependence on irrigation has not been without its negative environmental effects. Thus, the need to investigate the levels of accumulation of heavy metal concentrations in the edible parts of some cultivated vegetables irrigated with Ex – Tin Mining water in the area.

2. Materials and Methods

2.1. Study Area

The study was carried out in Barkin - Ldai Local Government Areas of Plateau State Figure 1. The study areas lie between latitude 9°30' 40''N to 9°33' 20'' and longitude 8°53'20''E to 8°54'40''E. The study area played host to a lot of mining activities by foreign companies which rendered the area derelict with numerous waste dumps and ponds. Soil and vegetables samples were collected through stratified random sampling method from four different farms each irrigated with tin mining ponds pond water.1kg of each of the vegetable samples including carrot, cabbage, garden egg, spinach, pepper and tomato from each stratum was collected. Three replications of each of these samples were analyzed for their heavy metals concentration using Flame Atomic Absorption Spectroscopy (FAAS).

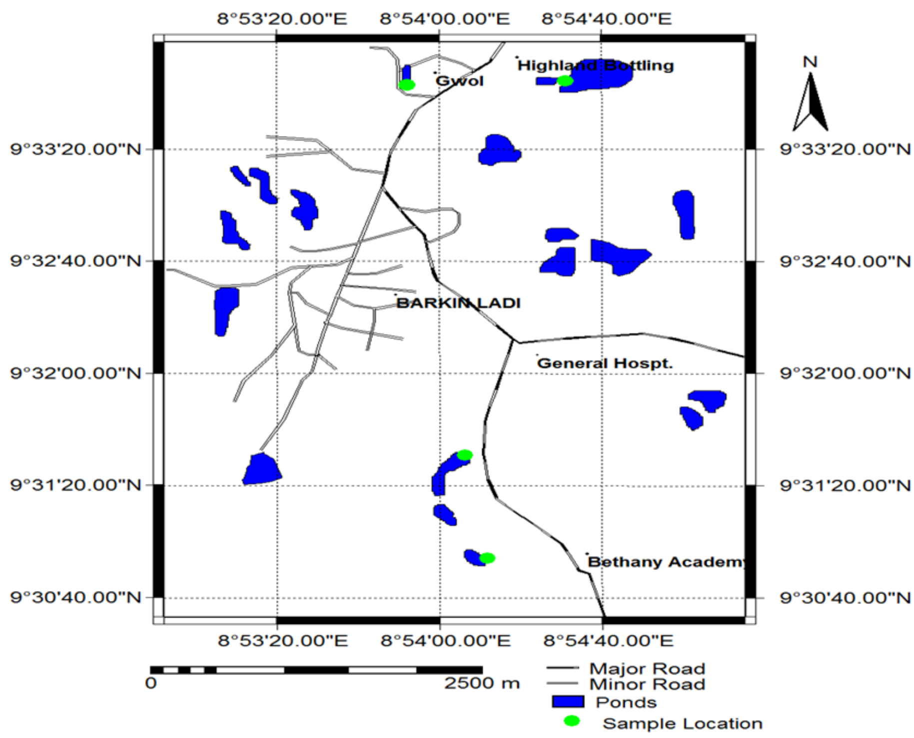

Figure-1. Map of Barkin – Ladi local government area showing study ponds.

2.2. Soil Sampling and Preparation

Soil samples were obtained from four farms each irrigated with tin mining pond water in the study farms viz: B_1 = Opp. Bethany Acad. B_2 = Hosp. Raod, B_3 = Gwol, B_4 = Behind Highland Bottling Company. The soil samples was collected at depth ranging between 0 - 20 cm using a steel soil auger and kept in tagged polythene bags. The soil samples were air-dried and sieved to <0.25 mm, then stored in desiccators prior to analysis of heavy metals. 5g of dried and sieved subsoil sample was taken into 100 mL of conical flask. 20 mL of 1:1 HNO_3 was added to conical flask and covered with a watch glass. Then the sample was evaporated to 5 to 8 mL on a hot plate. After cooling, 5 to 10 mL of $HClO_4$ and 20 mL of metal-free distilled water 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 transferred to a 100 mL volumetric flask and make up to mark with metal-free distilled water [22]. The concentrations of Pb, Cr, Cu, Cd, Zn, Mn and As were be determined by Atomic Absorption Spectrophotometer (FAAS. PG990).

2.3. Contamination Factor (CF)

The contamination factor was determined to express the level of metal contamination in surface soil and vegetables. The contaminant factor is calculated using the following formula:

$$CF = \frac{Cmetal}{Cbackground} \quad (1)$$

where: C_{Metal} is the concentration of a given metal in the soil and $C_{Background}$ is a metal concentration of a control soil sample. The CF value for describing the contamination levels is summarized in Table 1.

Table-1. Level of contaminant based on (CF) values.

CF values	Contamination remark
< 1	No contamination
1 – 2	Suspected contamination
2 – 3.5	Slight contamination
3.5 – 8.0	Moderate contamination
8.0 – 27	Severe contamination
> 27	Extreme contamination

Source: Sutherland [23].

2.4. Collection and Preparation of Vegetables for Analysis

The following vegetables were collected and analysed during dry and rainy season: Carrot (*Daucus carota subsp. Sativus*), family: Apiaceae; Spinach (*Spinacia oleracea L.*), family: Amaranthaceae and Tomato (*Lycopersicon Esculatum L.*), family: Solanaceae, cabbage (*Brassica oleracea*), red pepper (*Capsicum anum*) and Garden Egg *(Solanum melongena)*, respectively. The vegetables (mature) samples were collected randomly from the both farms treated. Healthy vegetables were collected carefully and washed thoroughly with tap water followed by distilled water and thereafter, kept on refrigerated under suitable condition analysis. The vegetables were cut into pieces with a stainless knife and dried at laboratory temperature and then powdered with mortar pestle before digestion to determine the heavy metals concentrations.

2.5. Plant Samples Digestion for Metal Analyses

One gram of each milled homogenized sample were weighed using a digital weighing balance into a conical flask. Exactly 5 mL of 60% hydrochloric acid (HCl) and 10 mL of 70% nitric acid (HNO_3) was added into the weighed samples. The sample mixture was digested with moderate heat (50°C) on a hot-plate until white fumes evolved, making it brownish solution. The heat was intensified further for few minutes to expel off 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 (11 µm) into a dispensed transparent plastic container that is clean with detergent and treated successively with HCl and rinsed with deionized water. The filtered sample was left to stand for few minutes for the aspiration of the element. The digested samples was then analyzed for the concentrations of; lead (Pb), manganese (Mn), chromium (Cr), cadmium (Cd), zinc (Zn), cupper (Cu), iron (Fe) and arsenic (As) using Atomic Absorption Spectrophotometer (AAS).

2.6. Statistical Analysis

Descriptive statistics viz., mean, standard error, standard deviation, minimum and maximum values of parameters are measured.

2.7. Karl Pearson's Coefficient of Correlation

Coefficient of correlation (r) is a quantitative measure of the correlation between two variables. The correlation coefficient is measure of correlation is based on arithmetic mean and standard deviation. This method can be used to measure correlation for individual series as well as for grouped data. The following equation is used for getting Pearson's coefficient (r) is:

$$r = \sum \frac{\left(\bar{X} - X\right)\left(\bar{Y} - Y\right)}{nSxSy} \quad (2)$$

where, r = coefficient of correlation, X = variable X, $\bar{X}$ = mean of variable X.
Y = variable Y, $\bar{Y}$ = mean of variable Y, n = number of pairs of variables.
Sx= SD of variable X, and Sy = SD of variable Y.

3. Results and Discussion

3.1. Heavy Metals in Soil

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 dynamic phenomenon in the soil and occurring continually is regulated by physical, chemical and biological processes and interactions between them. As a result it is found that any form is not stable for long time. In this study total content of soil Pb, Cu, Cd, Zn, Cr, Fe, Mn and As are considered which are depicted in

Lead (Pb): The mean concentration of Pb was 67.9±8.2 mg/Kg for the four different farm soil irrigated with tin mining pond. The highest concentration of 80.6 mg/Kg was observed in farm B_2 with the lowest 59.2 mg/Kg in farm B_1. The trend of the concentrations in the four different farms was $B_2 > B_3 > B_2 > B_4 > B_1$. This result showed similar trend of increased in Pb concentration in the soil irrigated with tin mining pond water. It was observed that Pb is positively correlated with Zn in dry season and negatively with Cu, Cr and Fe while in rainy season Pb is positively correlated with Fe. The reported values are within he prescribed safe limit of irrigation soil [24] standard limits. The value of Pb obtained in this work is higher compared with that reported in Kassa Ropp Barkin – Ladi [25]. Similar work done revealed Pb concentration in soil to range from 1 – 58 mg/Kg Mahmood and Malik [26]. Ratul, et al. [27] reported 28.13 mg/Kg in agricultural soil irrigated with contaminated river water lower than the concentration reported in this study.

Pb in soil treated with mining pond water is positively correlated with Mn and As in dry season and rainy season but a significant positive correlation is showed between Pb and available phosphorus in the treated soil collected during rainy season. The study showed the significant difference ($p < 0.05$) in the Pb content of the treated soils collected in both seasons. The Pb enrichment in the mining pond water irrigated soils as compared to ground water irrigated soils are collaborated with the findings of 15.4 ±6.6 mg/Kg and 9.31 ±2.2 mg/Kg [26],[28].

Copper (Cu): The mean value of Cu in mining pond water treated soil collected was 20.3mg/Kg and the highest value of 27.2 mg/Kg was obtained in farm B_1 with the lowest 15.6 mg/Kg at farm B_2. This result is lower compared to the findings 42.0 – 111.6 mg/Kg reported [3] which recorded extremely high concentrations of copper at industrial sites, and the also the reported 69.01 mg/Kg in agricultural soil irrigated with contaminated river water [27]. The Cu concentration of the soil irrigated with tin mining pond water is within the safe limit for cultivation [24]. The trend of Cu in the soil sample farms is in the order of $B_1 > B_4 > B_3 > B_2$, respectively. The metals contents in both soil irrigation with mining pond water also corroborated with the findings of Henry, et al. [29],Singh, et al. [5].

Cadmium (Cd): The concentration of Cd in the mining pond water treated soil with tin mining pond water in both sites studied shows a mean of 0.94 ± 0.4 mg/Kg. The highest concentration was obtained in farm B_1 1.17 mg/Kg and the lowest 0.28 mg/Kg at B_4. The concentration obtained in this work for soil treated with tin mining pond water agrees with the 0.965 mg/Kg reported [27] in agricultural soil irrigated with contaminated river water. Comparing with the safe limit of Cd in the soil it is found that both farm soils are within the prescribed standards of 3.0 mg/Kg set [30],[31]. Cadmium concentration in soil was relatively high, this may be attributed to applications of fertilizers and other farming practices including used of pesticides. Generally, the high concentrations of metals in this area could also be as a result of the tin mine activities, wastes dumped and metals availability in the earth crust.

The treated soil does not show any significant correlation with other parameter at the significant difference ($p < 0.05$). In this study Cd concentration in both tin mining pond water irrigated farm soils are lower compared to the literature values reports of 15.38±6.6 mg/Kg, 3.54±0.6 mg/Kg and 9.91±1.1 mg/Kg [26],[25],[32] respectively.

Zinc (Zn): The mean concentration of Zn in the mining pond water treated farm was 68.87 ± 18.4 mg/Kg. The highest concentration obtained was in farm B_2 soil 94.8 mg/Kg and lowest at B_3 soil 54.3 mg/Kg. From the concentration of Zn obtained in the soil irrigated with tin mining pond water, it is clear that the water has potential for the development of Zn enrichment. Both the soil samples analyzed has been found to be enriched with more Zn. The Zn concentration in both studied farm soils is within the safe limit of 200mg/Kg prescribed [31]. The Zn concentration in the wastewater irrigated soil reported in this study is in agreement with wastewater irrigated soil concentrations of 50.80 ±28.6 mg/Kg published [26] and reported concentration of 45.73 mg/Kg [27] 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 [28].

Chromium (Cr): The soil samples that are collected has a mean Cr concentration in mining pond water treated soil as 12.5 ±4.1 mg /Kg. It was observed that Cr in both farm soils, the highest concentration was found in farm B_1 soil 14.5 mg/Kg and lowest in B_2 soil 11.1 mg/Kg. The result reported in this study is lower compared with 22.9 mg/Kg reported by and 20.01±11.3mg/Kg [15], [26] and 54.2 mg/Kg reported in Kassa Ropp for similar tin mining soil and 69.75mg/Kg reported by Daniel, et al. [25], Ratul, et al. [27] in agricultural soil irrigated with contaminated river water. However, the low value obtained may be as attributed to leaching of metals beneath the soil. The Cr concentration in soil of both plots irrespective are within the 150 mg/Kg safe limit standard [30].

The study also showed the significant difference ($p < 0.05$) in the Cr content of treated soils collected in both seasons.

Iron (Fe): The soil sample irrigated with tin mining pond water during at the various sampling farms has mean concentration of 491.48 ±28.5 mg/Kg. Higher concentration of Fe were observed in the soil around farm B_1 526 mg/Kg and the lowest farm B_2 478 mg/Kg mining ponds, this may be as a result of the washing of mining piled dumps by runoff water during rainfalls. In the same vain Fe correlated negatively with Mn and As. The results show that iron (Fe) is the most abundant essential metal in both soil and vegetable samples, samples. The trend of concentration of Fe in the farm soils analyzed is in the order of $B_1 > B_4 > B_3 > B_2$. 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 anthropogenic source of Fe, which allows the percolation of Fe to the soil depths rather the surfaces. Boamponisem reported 14.08 mg/K lower values of Fe as compared to this work [32].

Manganese (Mn): The soil irrigated with tin mining pond water in both farms showed a of 18.1 ±1.3 mg /Kg, with the highest concentration obtained in farm B_4 soil 19.8 mg/Kg and the lowest at B_1 soil 16.3 mg/Kg. The trend in concentration in the farms soil is in the order of $B_4 > B_3 > B_2 > B_1$. This variation in concentration of Mn may be attributed to accumulation washing from different places such as roads, ashes from burn vegetation washed down by rainfall. The concentration of Mn reported in the soils studied is lower compared to limit of 80.0 mg/Kg prescribed by USEPA [31]. Increased Mn content in the mining pond water irrigated soils as compared with ground water irrigated soils agrees with findings of Mahmood and Malik [26].

Arsenic (As): The mean concentration of As in tin mining pond water treated soil collected from both farms was 146 ±23 mg/Kg. The highest concentration was recorded in B3 soil 174 mg/Kg with the lowest obtained in B1 soil 114 mg/Kg. The level of concentration of As in the farms is in the order of $B_3 > B_4 > B_2 > B_1$. The concentration of As recorded in this work is higher compared to the mean total arsenic concentrations of 50 – 60 mg/kg recorded for agricultural soils treated with arsenical pesticides [33],[34]. The result shows that there is accumulation of As in the soil as a result industrial wastes and pesticide applications which might increase concentrations. The As level in the irrigated soils is within the safe limit for cultivation. As, show positive correlation with Mn Cr and Pb. Naturally elevated levels of arsenic in soils may be associated with geological substrata such as sulfide ores therefore, anthropogenic contaminated soils can have several concentrations of arsenic. Arsenic concentrations of up to 27 000 mg/kg were reported in soils contaminated with mine or smelter wastes [35]. Soil on agricultural land treated with arsenical pesticides may retain substantial amounts of arsenic [34].

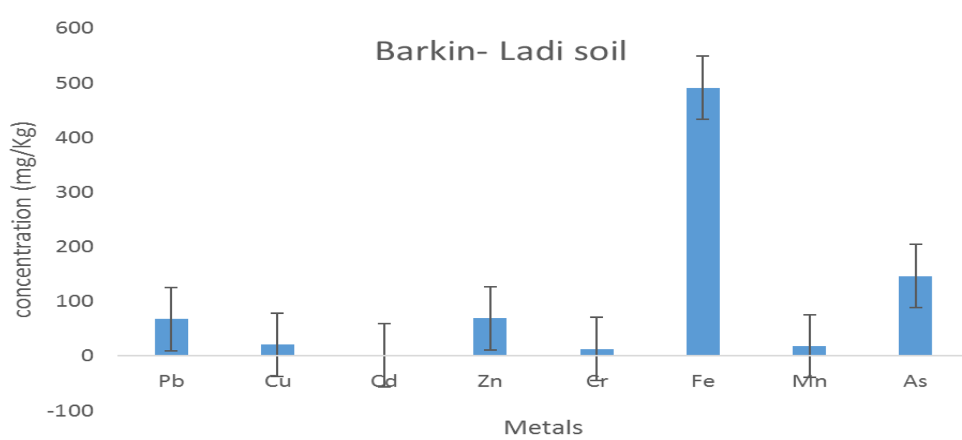

Figure-2. Mean Heavy metal concentration in soil irrigated with tin mining pond water (mg/Kg).

Table-2. Contamination of heavy metals for soil at different irrigated soil.

Metals	Bethany academy (B_1)	Hospital road (B_2)	Gwol (B_3)	Highland bottling company (B_4)
Pb	1.26	2.25	2.37	1.32
Cu	0.69	1.67	1.32	1.27
Cd	3.53	3.39	4.15	3.84
Zn	1.08	2.14	2.18	1.37
Cr	1.52	2.93	2.35	1.09
Fe	1.39	1.26	1.38	1.14
Mn	1.33	0.30	1.36	0.99
As	1.02	1.31	1.22	1.33

3.2. Contamination Factor (CF) of Heavy Metals in Soil

Contamination factor (EF) of heavy metals in the soil was calculated with help of the formula provided [36]. Soils collected from the cultivated soils' shows variation in metal concentration. Soils collected from the various farms of the study sites shows sequence of contamination in descending order as:

Cd > Zn > Pb > Cr > Cu > As > Fe > Mn.

Based on the contamination categories as proposed [23] it is found that soils irrigated with tin mining pond water were suspected to contamination with Cr, Pb, and Zn. The rest of the metals exhibit the minimal deficiency of mineral contamination in the soil and slight contamination was observed in the soil with Cd in all farms studied.

According [37] contamination values between 0.5 and 1.5 indicate the metal is entirely from the crust materials or natural processes, whereas contamination values greater than 1.5 suggest that the sources are more likely to be anthropogenic. Higher transfer coefficients reflect high soil contents or greater potentials of plants to absorb metals and bio-accumulate into tissues [38]. However, low transfer coefficients have been reported to indicate strong sorption of the metals to soil colloids [39]. Contamination factor (CF) of heavy metals in the irrigated soils is also highlighted as Cd (2.46) > Cr (2.43) > Zn (1.67) > Cu (1.36) > Pb (1.31) [40].

Table-3. Mean ±SD concentration of heavy metals in vegetables (mg/Kg).

Metals	Vegetables					
	Tomatoes	Garden egg	Pepper	Cabbage	Carrot	Spinach
Pb	0.491±0.11	0.396±0.05	0.307±0.26	0.164±0.03	0.465±0.02	0.455±0.04
Cu	0.071±0.01	0.076±0.01	0.065±0.00	0.065±0.01	0.090±0.01	0.062±0.01
Cd	0.009±0.00	0.006±0.01	0.006±0.00	0.005±0.00	0.022±0.01	0.014±0.01
Zn	0.376±0.04	1.104±0.08	0.395±0.02	0.184±0.02	0.913±0.06	0.448±0.03
Cr	0.154±0.03	0.116±0.00	0.106±0.01	0.109±0.01	0.148±0.02	0.147±0.03
Fe	1.551±0.21	1.170±0.02	1.489±0.03	1.489±0.07	1.647±0.14	1.554±0.21
Mn	0.454±0.39	0.825±0.11	0.177±0.01	0.166±0.01	0.791±0.15	0.115±0.01
As	0.076±0.01	0.043±0.01	0.033±0.02	0.028±0.01	0.466±0.39	0.046±0.00

3.3. Heavy Metals Accumulation in Cultivated Vegetables

Tomato: The result shows that Pb concentration in tomatoes is 0.49±0.1 mg/Kg. The values obtained are similar to the value 0.26 – 0.70 mg/ Kg Mahmood and Malik [26] and 1.15±0.29 mg/K reported values [41]; in a research on the level of As, Cd, Cr, Hg and Pb in soil and some vegetables which showed concentrations above maximum permissible limit and standard value. It 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 [42]. Higher concentration of 10. 75 mg/Kg are also reported in wastewater irrigated tomatoes [43].

The mean concentration of Arsenic was 0.076mg/Kg. This concentration is high compared to 0.06±0.02 mg/Kg reported [44] and 0.62±0.19 mg/Kg [41]. The high value of Arsenic in might be due the usage of arsenic containing chemicals such as pesticides and herbicides (calcium arsenate, cupper acetoarsenate and lead hydrogen arsenate). It was reported that these were used in pig and poultry feeds which in turn introduce arsenic into the soil and plants as chicken dug is used as fertilizers [45].

The Cr concentrations were also high in the study areas, with a mean of 0.15 mg/Kg. The concentration of Cr obtained in this study is lower compared to 0.66 mg/Kg reported in similar studies [46],[47].

Mn has a mean concentration of 0.45±0.39 mg/Kg in the tomatoes cultivated with tin mining pond water in the various farms studied. However, the might have been due washing by runoff water from the immediate vicinity since several anthropogenic processes took place and tin mining is still occurring in small scale by illegal miners. This is agree with the 0.12 mg/L reported on the study of vegetables in Southern Turkey [48]. The high concentrations of some of these metal in the areas could be as a result of the closeness of the mining ponds to major traffic highways. Other metals such Cu, Zn, and Fe, has concentrations of 0.071±0.01, 0.376±0.04 and 1.55±0.21, respectively.

Table-4. Pearson's correlation coefficient matrix (Mean) concentration of heavy metals in tomatoes.

	Pb	Cu	Cd	Zn	Cr	Fe	Mn	As
Pb	1.000							
Cu	-0.750	1.000						
Cd	0.743	-1.000	1.000					
Zn	0.906	-0.399	0.389	1.000				
Cr	-0.667	0.993	-0.994	-0.288	1.000			
Fe	-0.410	0.911	-0.915	0.015	0.953	1.000		
Mn	0.869	-0.325	0.315	0.997	-0.211	0.095	1.000	
As	0.365	-0.890	0.894	-0.064	-0.937	-0.999	-0.143	1.000

Statistically (p-value < 0.05). Pb is positively correlated with Cd, Zn and Mn while Zn with Mn. A positively correlation was also notice between Cd and As, and also Cr is negatively correlated with Cd and As. The order of metal concentration in tomatoes in this work is; Fe > Mn > Zn > Pb > Cu > Cr > As > Cd. Heavy metal accumulation in tomato due to long-term wastewater irrigation was also highlighted [29], [43],[49].

Garden egg: The mean concentrations of each heavy metals in the three farms shows that Pb 0.40 ±0.05, Cr (0.12 ±0.00) and Mn (1.17±0.02) As (0.83 ±0.11) mg/Kg were higher than the standard permissible limit [50] respectively. The concentration of Cu 0.076±0.01 below the permissible standard value of 0.7mg/Kg in both garden egg irrigated with tin mining pond water while the concentration Fe and Cd are lower compared to other metals standards. The order of heavy metals accumulation in garden egg was Fe > Mn > Pb > Zn > Cu > Cr > As > Cd. Pearson's correlation shows that in garden egg Pb is positively correlated with Zn and Mn, while Cu is positively correlated with Cr, and Cd negatively correlated with Cr. The results obtained in this study were similar to the reported studies many scholars [43],[51],[52] who also reported high levels of Zn (3.91) and Cd (1.56) mg/Kg in wastewater irrigated garden egg in Kaduna, Nigeria.

Table-5. Pearson's correlation coefficient matrix (Mean) concentration of heavy metals in garden egg.

	Pb	Cu	Cd	Zn	Cr	Fe	Mn	As
Pb	1.000							
Cu	-0.750	1.000						
Cd	0.743	-1.000	1.000					
Zn	0.906	-0.399	0.389	1.000				
Cr	-0.667	0.993	-0.994	-0.288	1.000			
Fe	-0.410	0.911	-0.915	0.015	0.953	1.000		
Mn	0.869	-0.325	0.315	0.997	-0.211	0.095	1.000	
As	0.365	-0.890	0.894	-0.064	-0.937	-0.999	-0.143	1.000

Pepper: The mean concentration of the various heavy metals in pepper irrigated with tin mining pond water was Pb (0.307±0.26), Cu (0.065±0.00), Cd (0.006±0.00), Zn (0.395±0.02) Cr (0.106±0.01), Fe (1.489±0.03), Mn (0.177±0.01) and As (0.033±0.02). The concentration of Cd was slightly lower in all the study areas. The order of concentration of the heavy metals in pepper cultivated with tin mining pond water was Fe > Mn > Pb > Cu > Zn > Cr > As > Cd. The concentrations of Mn, Cr, Pb and Cd in pepper in the studied areas have crossed the prescribed safe value [30],[50] respectively. The high concentration of this 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 as Mn (19.1±1.7) mg/Kg accumulation in vegetables grown on farmlands irrigated with treated sewage water in Ghana [53]. 1.15±0.29 mg/Kg accumulation of Cd in pepper is also being reported [41]. Pb and Cu correlated positively Cr, Mn and As, while Cd correlated positively with Mn and As and Cr negatively correlated with As. Heavy metals concentration in both sites vegetables showed significant level ($p < 0.05$) accumulation except Cd ($p = 0.05$). Dorcas High levels of heavy metals are also reported vegetables irrigated with wastewater from mines and industrial discharges to soils [54],[55],[56],[57].

Table-6. Pearson's correlation coefficient matrix (Mean) concentration of heavy metal in pepper (mg/kg).

	Pb	Cu	Cd	Zn	Cr	Fe	Mn	As
Pb	1.000							
Cu	-0.751	1.000						
Cd	0.944	0.998	1.000					
Zn	-1.000	-0.969	-0.952	1.000				
Cr	-0.873	-0.707	-0.664	0.861	1.000			
Fe	0.763	0.910	0.933	-0.779	-0.351	1.000		
Mn	0.907	0.987	0.995	-0.917	-0.587	0.964	1.000	
As	0.907	0.980	0.966	-0.999	-0.834	0.809	0.936	1.000

Cabbage: The mean concentration of heavy metals in the studied cultivated cabbage irrigated with tin mining pond water was found to be Pb (0.164±0.03), Cu (0.065±0.01), Cd (0.01±0.00), Zn (0.18 ±0.02), Cr (0.11±0.01), Fe (1.49±0.07), Mn (0.17±0.01) and As (0.03±0.01) mg/Kg. The concentration of metals in cabbage irrigated with tin mining pond water is lower compared to the reported literature of 0.22±0.2 mg/Kg and 6.25±1.2 mg/Kg 1.61±0.2 [56],[58], [59] mg/Kg). Similar studies conducted show order of concentration of the heavy metals in is: Fe > Mn > Pb > Zn > Cr > Cu > As > Cd [29]. It was therefore, noted that some of metals that are high in cabbage cross the standard permissible limits FAO/WHO.

The high levels of these metals in this vegetable might be as a result of the use of pesticides and herbicides and irrigated with tin mine water [60]. This also agrees with the findings that, the application of large volumes of partially treated or untreated wastewater in some parts of Africa has adversely affected both surface water bodies and the urban and peri-urban farmers using these water bodies as sources of irrigation [61]. The Pearson's correlation shows that Pb correlated positively with Cu, Mn, As, and negatively correlated Cr. Cd is positively correlated with Mn, As and negatively correlated with Cr at ($p > 0.05$).

Table-7. Pearson's correlation coefficient matrix (Mean) concentration of heavy metals in cabbage.

	Pb	Cu	Cd	Zn	Cr	Fe	Mn	As
Pb	1.000							
Cu	0.993	1.000						
Cd	-0.148	-0.034	1.000					
Zn	0.958	0.984	0.143	1.000				
Cr	-0.754	-0.824	-0.538	-0.911	1.000			
Fe	-0.994	-0.974	0.260	-0.919	0.674	1.000		
Mn	0.932	0.884	-0.497	0.788	-0.464	-0.967	1.000	
As	0.999	0.992	-0.163	0.953	-0.744	-0.995	0.937	1.000

Carrot: The heavy metals in the carrot analyzed from the sampled farms shows that the concentrations are higher in all studied metals. The metals studied crossed the safe limit of European Union (EU) [30]; FAO/WHO [50] limit with the exception of Cu, Zn, and Fe others were not safe for human consumption as their concentrations were above the maximum permissible limit, 0.30mg/kg. The mean concentrations of Pb (0.46 mg/Kg) and As (0.47 mg/Kg) were higher compared to other toxic metals in carrot The studied metals are in order of their descending trend: Fe > Zn > Mn > As> Pb > Cr > Cu >Cd. studies showed that cadmium (Cd) had mean concentration of 0.24 mg/kg in carrots in Barkin - Ladi Haipang compared [54] with the result of 0.02mg/Kg recorded in this work. Several results have been reported of Cd in carrot due to irrigation with wastewater [26],[62],[63]. Pb correlated positively with Cr and negatively with Mn. Cd and Cr showed negative correlation in significant level of ($p < 0.05$).

Table-8. Pearson's correlation coefficient matrix (Mean) concentration of heavy metals in carrot.

	Pb	Cu	Cd	Zn	Cr	Fe	Mn	As
Pb	1.000							
Cu	0.993	1.000						
Cd	-0.768	-0.687	1.000					
Zn	0.662	0.569	-0.989	1.000				
Cr	0.923	0.872	-0.955	0.899	1.000			
Fe	0.399	0.289	-0.894	0.951	0.721	1.000		
Mn	-0.703	-0.615	0.995	-0.998	-0.922	-0.933	1.000	
As	-0.285	-0.395	-0.396	0.530	0.105	0.765	-0.481	1.000

Spinach: The concentration of all the metal studied in all sites were found to have high metals in spinach but others show lower values. The mean concentration of spinach was Pb (0.46 ±0.04) Cu (0.06±0.01), Cr (0.014±0.01), Zn (0.45±0.03), Cr (0.15±0.03), Fe (1.55±0.21). Comparing the concentration heavy metals studied in spinach, it is found that values obtained for Pb are lower than the findings of 2.9±1.2 mg/Kg 1.50±0.1 mg/Kg,15.1 mg/Kg 2.78 mg/Kg, 3.31mg/Kg [26],[32],[56],[64],[65]. The concentration of Cr and Cd in agricultural soil irrigated with contaminated river water are far higher than the value reported in this work [4],[27],[39],[66].

Comparing with the prescribed standards it is found that Pb, Cr, As, Mn and Cd content in spinach have crossed safe limit [24],[30]. However, the major sources of vegetable contamination with heavy metals might be due to the waste water irrigation, solid waste disposal, sludge applications, vehicular exhaust. Excessive accumulation of heavy metals in agricultural soils through the use of agrochemicals and by other sources may lead to elevated heavy metal up-take by vegetables and thus affect food quality and safety [66]. Statistically heavy metals content in spinach in shows significant ($p < 0.05$). Pb is positively correlated with Cr and negatively correlated with Mn and As. Wastewater induced heavy metals enrichment in spinach was also studied [4],[39]. 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 [7]. It is worthy of note that low concentrations of Fe in the vegetable samples relative to its abundant availability in the soils, can be attributed to; low absorption of Fe by the tissues of the vegetable samples, possible leaching of Fe from the soil surface and runoff during rainfall.

Table-9. Pearson's correlation coefficient matrix (Mean) concentration of heavy metals in spinach.

	Pb	Cu	Cd	Zn	Cr	Fe	Mn	As
Pb	1.000							
Cu	-0.202	1.000						
Cd	0.597	-0.906	1.000					
Zn	-0.771	0.780	-0.971	1.000				
Cr	0.988	-0.182	0.581	-0.758	1.000			
Fe	0.807	-0.741	0.955	-0.998	0.795	1.000		
Mn	-0.796	-0.431	0.009	0.229	-0.809	-0.286	1.000	
As	-0.882	-0.283	-0.149	0.380	-0.891	-0.434	0.987	1.000

3.4. Conclusion

From the present study it is noted that tin mining pond water irrigation practice is not suitable for cultivating edible vegetables especially those that are consumed regularly. Because excess heavy metals are considered as toxic elements due to accumulation in the biological systems and subsequently interfere in metabolic activity of organ specific. In this study the vegetables cultivated with this water are not safe for consumption. So, emphasis should be made on the use of good quality irrigation water for the cultivation of vegetables which have less accumulation potential.

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