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Health Risk Assessment of Heavy Metals in Consumption of Vegetables Irrigated with Tin Mine Pond Water in Jos – South, Plateau State

G. M. Mafuyai, S. Ugbidye and G. I. Ezekiel

ABSTRACT

The water range from Pb (1.439 – 1.715), Cu (0.234 – 0.377), Cd (0.838 – 1.346), Zn (0.448 – 1.110), Cr (0.144 – 0.794), Mn (0.777 – 2.011) and As (0.584 – 1.341) mg/L. The range in soil was Pb (67.5 – 120), Cu (8.51 – 32.5), Cd (0.21 – 1.72), Zn (70.8 – 85.6), Cr (15.8 – 29.5), Mn (14.6 – 19.1) and As (52.0 – 198) mg/kg and in the vegetables in the range of Pb (0.177 – 0.545), Cu (0.073 – 0.748), Cd (0.005 – 0.019), Zn (0.264 – 0.915), Cr (0.089 – 0.158), Mn (0.162 – 0.253) and As (0.032 – 0.245) mg/kg. The study shows that the transfer coefficient of the heavy metals to vegetable was less than one (< 1). The estimated daily intake (DIM) of heavy metals from vegetables irrigated with tin mine pond water were in the order: Cd > Zn > Mn > Cr > Cu > Pb > As. The health risk index (HRI) of all the studied heavy metals indicated that all vegetables were safe with no risk to human health except for Cd. health risk assessment of heavy metals in consumption of vegetables irrigated with tin mine pond water in Jos - South, Plateau State was investigated. The concentration of heavy metals in the tin mine pond.

Keywords: Contamination, Health Risk Index, Heavy Metals.

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I. INTRODUCTION

Heavy metals contamination is a major problem of our environment and they are also one of the major contaminating agents of our food supply. This problem is a concern all over the world, especially in developing countries. The tradition of growing vegetables within and at the edge of industrial mine areas of cities is very old. It is revealed that most of these cultivated lands are contaminated with heavy metals contributed through mining waste water irrigation [1].

Tin is said to be one of the oldest mineral resources known to man as its strategic importance was recognized as far back as some 300 years ago when its hardening effects on copper was discovered [2]. Since then, tin ore has been mined in several parts of Nigeria including Zaria, Kano, Bauchi, Ilesha and Jos provinces, with over 80% of the production coming from the Jos Plateau [3]. Mining gives rise to large amount of excavated overburdens dumped on the surface (mine spoil) and deep mine ponds; this may contain various minerals and heavy metals, some of which are toxic in nature and affect the environment when their concentration exceeds the permissible levels. Surface runoff and wind erosion from mining sites could cause increase in concentration of the heavy metals in local biota, and have more significant effect on the ecosystem which may lead to geo-accumulation and subsequent bio-accumulation and bio-magnifications in the food chain [4].

Water is an essential component of life, fresh water constitute about 3% of the total water on the earth surface, only 0.01% of this fresh water is available [5], with two thirds of the earth's surface covered by water and the human body consisting of 75% of it, it is evidently clear that water is one of the prime elements responsible for life on earth. Regrettably, even this small portion of fresh water is under pressure due to anthropogenic sources due to rapid growth in population and industrial activities [6].

Scarcity of fresh water is the main driving force towards the utilization of tin mine pond water for irrigating vegetables. Long-term mine pond water irrigation practice enriched heavy metals in soil thus; vegetables cultivated in metals enriched soil accumulate heavy metals in their tissues [7]. Heavy metals are the main pollutants and elements of risk in drinking water [8]. Investigation on water contamination by heavy metals has become the prime focus of environmental scientists in recent years [9].

Soil contamination with metals is a primary route of toxic elements exposure to humans as they can enter the human body by consumption of contaminated food crops, water or inhalation of dust [10]. It is evident that more than 70% of dietary intake of heavy metals is contributed to food chain [11]. The prolong consumption of foodstuff contaminated with heavy metals may lead to unceasing accumulation of toxins in the liver and kidney of humans resulting in disturbances of biochemical processes such as liver, kidney, cardiovascular, nervous and bone disorders [12], [13].

Vegetables are known to be good absorber of heavy metals from the soil and the danger lies in its ability to accumulate in the bodies of local residents [1]. Human and animal need a certain percentage of these elements that might happen on the part of the plant through the food chain [80]. The accumulation of heavy metals and metalloids in agricultural soils is of increasing concern due to the food safety issues and potential health risks as well as its detrimental effects on soil ecosystems [79].

A. Human Health Risk

Human health risk assessment is considered as the characterization of the potential adverse health effects of humans as a result of exposures to environmental hazards [13]. This process employs scientific tools to identify and measure a hazard, determine possible routes of exposure, and finally use that information to calculate a numerical value to represent the potential risk [14].

Mining wastewater used in irrigation induced heavy metals accumulation in vegetables and heavy metals associated risk assessment for consumers. Human are exposed to the risk through the consumption of vegetables contaminated with heavy metals. Most consumers are not aware with the source of the produce and the use of polluted irrigation water [24].

The health risk of heavy metals depends on the nature, concentration in vegetables, amount in vegetable consumed and so on. Health risk assessment of heavy metals in contaminated vegetables is extensively studied in developed countries [15], [16], [17], [18], [19] however, little information is available in Nigeria with very few published data on heavy metals Contamination in vegetables is available [7], [20], [21], [22].

A human health risk assessment involves four steps which are: hazard identification, dose-response assessment, exposure assessment, and risk characterization. Health risk assessment classifies elements as, carcinogenic or non-carcinogenic. The classification determines the procedure to be followed when potential risks are calculated. Non-carcinogenic chemicals are assumed to have a threshold; a dose below which no adverse health effects will be observed where an essential part of the dose-response portion of a risk assessment includes the use of a reference dose (RfD). Also, carcinogens are assumed to have no effective threshold. This assumption implies that there is a risk of cancer developing with exposures at low doses and, therefore, there is no safe threshold for exposure to carcinogenic chemicals. Carcinogens are expressed by their Cancer Potency Factor [82]. Environmental abatement is almost lacking due to lack of environmental management and un-operational environmental laws. Irrigation with tin mine pond water is a common practice in the peri- urban Jos - South Local Government Area in Plateau State, Nigeria [23].

The cultivation of vegetables crops with tin mine pond water is a common practice in Jos- South, Plateau State. Local farmers in the area uses the surface tin mine pond water to irrigate their agricultural fields for cultivation of vegetable crops. It has been reported that serious health problems can develop as a result of consumption of dietary foodstuffs contaminated with toxic heavy metals [83]. Therefore, the study is conducted to assess the heavy metal contamination in soil, resulted uptake by the vegetables and its eminent transfer to the food chain which assist in evaluating the related health hazards linked with.

II. Materials And Methods

A. Study area

The study areas lie between latitude 9°46'N to 9°50'N and longitude 8°52'E to 8°55'E. The areas played host to a lot of mining activities by foreign companies such British Mines Corperation Limited, Bisichi Jenta Limited, Gold and Base Corporation [24].

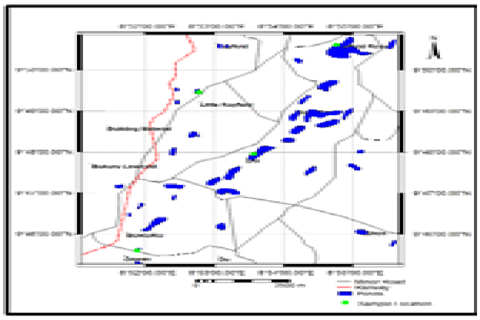

Fig.1 Map of Jos – South Showing Study Mined Ponds Sites

a) b) c) d)

Fig. 2. Typical (a), mining pond (b) irrigation of pump (c) garden egg farm (d) pepper farm.

B. Sampling and Determination of Heavy Metals in Tin Mine Pond Water

High-density polyethylene bottles were rinsed with metal-free detergent and soaked in 10% HNO_3 acid overnight and finally washed thoroughly with metal-free deionized water [25]. The bottles were used for collection of water samples from the tin mine ponds that were used in irrigating farms and taken to Chemistry Laboratory University of Jos, Nigeria and stored at 4 0C in a refrigerator.

About 100 mL of the water sample was taken into a 250 mL conical flask. Exactly 5 mL of conc. HNO_3 was added and covered with a ribbed watch glass and evaporated to 20 mL on a hot plate. After which 5 mL each of HNO_3 and

$HClO_4$ was added cooled beaker between additions. The sample was evaporated again on a hot plate until dense white fumes of $HClO_4$ just appeared. The Sample was then cooled, diluted with metal-free distilled water and then filtered through Whatman No. 42 filter paper. The Filtrate was transferred to a 50 mL volumetric flask and diluted to mark with metal-free distilled water. Reagent blank was prepared following same procedure using metal - free distilled water. The clear solution obtained after digestion was analyzed for lead (Pb), manganese (Mn), chromium (Cr), cadmium (Cd), zinc (Zn), cupper (Cu) and arsenic (As) by atomic absorption spectrophotometer (AAS). 2.3 Soil sampling and determination of heavy metals

Soil from the irrigated farms were collected by digging 0 - 20 cm depth, using a steel soil auger, non-soil particles were removed from the soil and the soil kept in tagged polythene bags. The soil samples were air-dried and sieved to < 0.25 mm, then stored in desiccators [26], prior to analysis of heavy metals. About 5 g of dried and sieved subsoil sample were taken into 100 mL conical flask and digested with 20 mL of 1:1 HNO_3 covered with a watch glass. Then the sample was evaporated to 8 mL on a hot plate. After cooling, 10 mL of $HClO_4$ and 20 mL of metal-free distilled water added. Then the sample was again evaporated to 10 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 [27]. The concentrations of Pb, Cr, Cu, Cd, Zn, Mn, and As, were determined using Atomic Absorption Spectrophotometer [28].

C. Collection of plant samples and digestion for metal analyses

The vegetables; garden egg (*Solanum melongena*), Spinach (*Spinacia oleracea L.),* family: Amaranthaceae and 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 and stored in a labelled polythene sampling bags. The samples 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 formed.

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 (HNO3) 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. The filtered sample were left to stand for few minutes for the aspiration of the element and then analyzed for heavy metals concentration using Atomic Absorption Spectrophotometer (AAS).

D. Quality control

The chemical used were purchased from MERCK Chemical Germany agent in Lagos Nigeria. Double deionized water was used for solution preparation and glassware were washed with 10% HNO_3. Standards were prepared for each metal from stock solution to calibrate the instrument. Precision and accuracy of analysis were checked through repeated analysis against NIST standard reference material SRM 1570A for vegetables, RM 1643E for water and SRM 2709 for soil for heavy metals.

E. Data Analysis

1. Transfers factor

Transfers factor (TF) was calculated to understand the extent of risk and associated hazard due to wastewater irrigation and consequent heavy metals accumulation in edible portion of test vegetables [29].The concentration of heavy metal in extracts of vegetables and soils on dry weight (DW) basis, respectively.

$$TF = \frac{C_{plant}}{C_{soil}} \qquad (1)$$

The ratio "> 1" means higher accumulation of metals in plant parts than soil [30]. If the transfer coefficient of a metal is greater than 0.50, the plant will have a greater chance of the metal contamination by anthropogenic activities [31].

2. Daily intake of metals (DIM)

The Daily intake of metals (DIM) to the exposure pathway of heavy metals to human through ingestion of vegetables grown on wastewater irrigated soils [32]. Moreover, the DIM in this exposure pathway was determined by the multiple of the concentration in the vegetable on dry weight basis.

$$DIM = \frac{C_{vegetable} \text{ x } C_{factor} \text{ x } C_{food\ intake}}{B_{average\ weight}} \qquad (2)$$

where $C_{vegetable}$, C_{factor}, $D_{food\ intake}$ and $B_{average\ weight}$ represents the concentrations of heavy metal in vegetables (milligrams per kilogram) on dry weight basis, conversion factor for fresh to dry weight of vegetables (0.085) [33], daily intake of vegetables (0.345 kg per person per day for adults) and average body weight (55.90 kg for adults), respectively.

3. Health risk index (HRI)

Health risk index (HRI) assessment of consumers from the intake of vegetable contaminated with metals is characterized by using HRI. If, HRI is less than 1, there will not be obvious risk for exposed population and vice versa. The HRI is obtained by dividing the daily intake of metals (DIM) by the reference oral doses (RfD).

$$HRI = \frac{DIM}{RfD} \qquad (3)$$

where

Reference oral doses (RfD) for Pb, Mn, Cr, Cd, Zn, Cu and As are 0.0035, 0.033, 1.5, 0.001, 0.30, 0.04, and 0.0003 mg/kg. If the value of HRI is less than 1 then the exposed population is said to be safe [34].

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III. RESULTS AND DISCUSSION

A. Heavy metals concentration in mine pond water (mg/L)

Lead (Pb): Lead in the mine pond water used in irrigating the agricultural fields show a mean concentration of 1.62 ± 0.1 mg/L However, the value obtained in this work is higher compared to that (0.08 mg/L) reported [35] and lower to that (3.18 mg/L) reported [36]. The value of Pb in both site studied are within the prescribed standard of irrigation [37]. Table 1 shows that the Pb concentration in tin mine pond positively correlated with Cd and negatively correlated with Cr. Higher lead concentration in the tin mine pond water agree with the findings of [18], [38], [39].

Copper (Cu): The mean concentration of Cu in tin mine pond water in the three studied areas 0.43 ± 0.01 mg/L (Fig. 2). The concentration of Cu in tin mine pond water exceeds the recommended limits prescribedfig by FAO/WHO [37]. In the tin mine pond water Cu positively correlated with Cd, Mn and negatively correlated with As (Table 1). The higher concentration of Cu in the tin mining pond water as compared with literatures agrees with the findings of other researcher viz., [18], [38], [40].

Cadmium (Cd): The mean concentrations of Cadmium in the tin mine pond water was 1.03 ± 0.21 mg/L. 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, [38] and the values agree with the findings of Boamponisem [41]. Considering the toxicity of Cd however, this study recorded a lower value compared with the study carried by Henry, [21], on one of the ex-mine ponds in Jos - South Plateau State. 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. Similar studies on irrigation water quality in Nigeria and abroad have reported slightly higher concentrations of Cadmium [42]. The concentration of Cd recorded in this analysis is above [37], [43] prescribed limits of 0.01 and 0.005 mg/L, respectively. The Cd content in the water show significant correlation with other heavy metals and display positive correlation with arsenic ($P > 0.05$) as presented in (Table 1).

TABLE 1: PEARSON'S CORRELATION COEFFICIENT MATRIX (MEAN) HEAVY METALS IN MINING POND WATER

	Pb	Cu	Cd	Zn	Cr	Mn	As
Pb	1.000						
Cu	0.454	1.000					
Cd	0.563	0.992	1.000				
Zn	0.261	0.300	0.315	1.000			
Cr	-0.725	-0.363	-0.440	0.453	1.000		
Mn	-0.478	0.565	0.456	0.030	0.294	1.000	
As	0.291	-0.670	-0.580	-0.413	-0.399	-0.921	1.000

Zinc (Zn): The mean concentration of Zn in mine pond water was 0.749 ± 0.31 mg/L. The mean value of Zn is quite high in both sites, compared FAO/WHO [37] prescribed standard for irrigation water. Related studies on irrigation water in Burkina Fasso, reported a mean concentration of 0.034 mg/L in groundwater [44], which is lower than the values recorded in this work. Similarly, Lente et al. also reported a mean concentration of 0.14 mg/L zinc in irrigation water in Accra, Ghana, which is in agreement with the values obtained in this study [45]. The concentration range of Zn, 0.34 – 1.39 mg/L were reported in different sources of irrigation water in Lahore, Pakistan [18]. The high concentrations of zinc recorded in this study could be due to weathering of geological materials and possibly small scale mining and runoff from farms treated with agrochemicals containing Zn [23].

Chromiun (Cr): The mean concentration of chromium in the tin mine pond water was 0.35±0.3 mg/L. The concentration of Cr in the tin mining pond water corroborated with the findings reported on similar work in Lahore, Pakistan [18], and the reported 0.38 mg/L in ex-mining pond in Plateau State [21]. Though the tin mining pond water showed higher Cr concentration compared to the prescribed standard limit by WHO/FAO and USEPA, the Cr concentration in the studied areas was lower compared to the 2.72 -14.04 mg/L and 1.05 mg/L reported by Brar [45], [42], respectively. Statistically, there was significant difference Cr in at 95% confidence limit.

Manganese (Mn): The mean concentration of was 0.50 ± 0.1 mg/L in the tin mine pond waters, Mn concentration was higher than the prescribed standards irrespective of the pond water studied. Similar reported high mean concentration of Mn 1.50±0.1 mg/L in sewage water used for irrigation in Asansol, West Bengal [42]. The Mn concentration tin mining pond water it is negatively correlated with As. ($p > 0.05$). The high levels of Mn observed in the water can be attributed to anthropogenic activities, particularly large scale mining and the activities of motorist that took place within the area. Mining in general is known to have an influence on the flux of metals from geological materials to the hydrosphere through dissolution of minerals [46]. Manganese concentration in mining pond water used for irrigation of crops agrees with these findings [39], [47].

Arsenic (As): The mean of As in the tin mining pond waters in the study areas showed a concentration of 0.94±0.4 mg/L. The concentration of As in this study is higher compared with 0.04 mg/L reported in sewage water used for irrigation in Northwest India [45]. Arsenic in water is mostly present as (As^{5+}), but in anaerobic conditions, it is likely present as (As^{3+}) WHO, [48]. Arsenic in drinking water is a global threat to health (United Nations International Children's Emergency Fund UNICEF, World Health Organization WHO [48]. 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 [48].

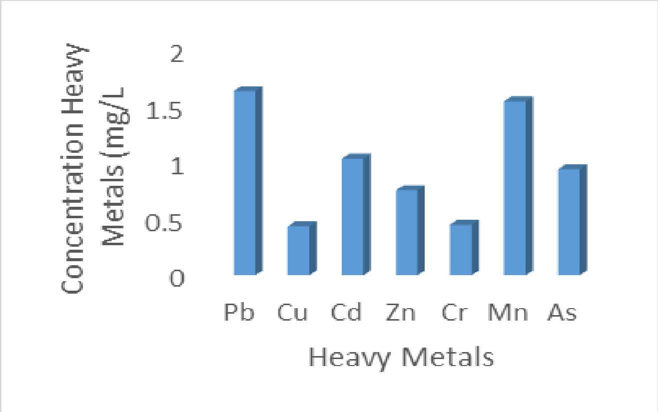

Fig. 3. Mean Concentration of Heavy metals in mine pond water (mg/L).

B. Heavy metals in soil irrigated with tin mining pond Water

Lead (Pb): The mean concentration of Pb obtained from the various sites was 83.0±13.3. The result shows that the concentration of Pb in both the study areas were slightly different and higher than the values obtained in Bokkos [23]. The concentration of Pb in the soil in respective of season and plots in the study areas is in the order of Doi >Zawan > Little Ray Field > Ray field Resort. All the reported values are above the prescribed 50 mg/kg of soil WHO,[49] standard limits. The value of Pb obtained agree with that reported by Daniel et al. in Kassa Ropp Barkin-Ladi [50]. It is also revealed that Pb concentration in agricultural soil irrigated with contaminated water vary with the concentration reported in this study [51]. Pb in soil treated with mining pond water is positively correlated with Cr and As. The study showed the significant difference ($p < 0.05$) in the Pb content of the treated soils collected in both seasons.

Copper (Cu): The mean value of Cu in mining pond water treated soil was 22.5±9.64 mg/kg, It is also observed that there is a significant different in the concentration of Cu in the sites studied. The Cu concentration of the irrigated soils is within the safe limit for cultivation. In it observed that Cu positively correlated with As. The metals concentration in both soil irrigation with mining pond water, corroborated with the findings [21].

Cadmium (Cd): The mean concentration of Cd in the mining pond water treated soil in both sites studied shows a value of 1.14±0.6 mg/kg. 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. [51] 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 the both season are within the prescribed standards of 3 – 6 mg/kg set by [48], [49], [52].

Cadmium concentration in soil was relatively high, Cd correlated positively Cr this may have been attributed to applications of fertilizers and other farming practices including used of pesticides. Generally, the high concentrations of metals in these areas could also be as a result of the tin mine activities, wastes dumped and metals availability in the earth crust. In this study Cd concentration in both irrigated soils are lower compared to the literature values 15.4±6.6 mg/kg and 3.54±0.6 mg/kg reported [18] [50].

Zinc (Zn): The mean concentration of Zn in the mining pond water treated soil during was 77.7±6.3 mg/kgfor both sites. From the value of Zn content in the tin mining pond water irrigated soil, 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 though within the safe limit of 200 mg/kg prescribed by USEPA and 300 mg/kg by WHO. The Zn concentration in the soil irrigated with tin mining pond water reported in this study is in agreement with wastewater irrigated soil concentrations published by Mahmood and Malik and reported concentration in agricultural soil irrigated with contaminated river water [51] but however, higher compared to the result of 3.9±0.1 and 6.03±1.7 mg/kg reported Tukura et al. [35] and Lente et al. [40], respectively.

Chromium (Cr): The soil samples collected and analyzed exhibited the mean Cr concentration of 21.8±6.5 mg /kg. The result reported in this study is in agreement with 22.9 mg/kg reported by Ghosh et al. [52] and 20.01±11.3 mg/kg [18]. The concentration obtained even though high, is lower than the value 54.2 mg/kg reported by Daniel et al. [53] in Kassa Ropp for similar tin mining soil and 69.75mg/kg reported by Ratul et al. [40] in agricultural soil irrigated with contaminated river water. However, the low value may be as attributed to leaching of metals beneath the soil. The Cr concentration in soil of both plots irrespective of sites are within the 150 mg/kg safe limit of EU standard [54].

Manganese (Mn): The soil irrigated with mining pond water during had a mean of 16.8±1.9 mg/kg. Variation of mean Mn concentration in soil is not high as the order was Zawan > Ray field Resort > Doi > Little Ray Field. The high Mn concentration may be attributed to accumulation washing from different places such as roads, ashes from burn vegetation washed down by rainfall.

Arsenic (As): The mean concentration of As in mining pond water treated soil was 135±56 mg/kg. The values showed 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 was far above the safe limit of 20 mg/kg prescribed by WHO, 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, anthropogenically contaminated soils can have several concentrations of arsenic [55]. Arsenic concentrations of up to 27 000 mg/kg were reported in soils contaminated with mine or smelter wastes [56]. Soil on 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 [57].

TABLE 2. PEARSON'S CORRELATION COEFFICIENT MATRIX (MEAN) HEAVY METALS CONTENT IN SOIL

	Pb	Cu	Cd	Zn	Cr	Mn	As
Pb	1.000						
Cu	-0.798	1.000					
Cd	0.138	-0.489	1.000				
Zn	0.369	0.140	0.156	1.000			
Cr	0.728	0.213	0.735	0.112	1.000		
Mn	-0.371	-0.068	-0.280	-0.992	-0.199	1.000	
As	0.823	0.996	-0.448	0.230	0.239	-0.161	1.000

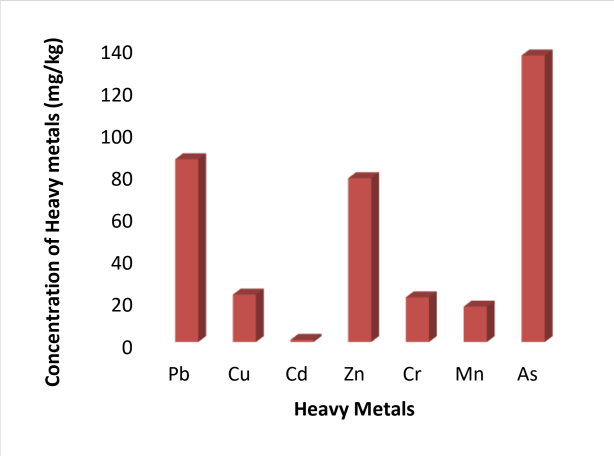

Fig. 4. Mean Concentration of heavy metals in soil irrigated with mined Pond Water (mg/kg).

C. Heavy Metals Accumulation in Vegetables Cultivated with Tin Mining Pond Water Tomato

Table 3 shows that the concentration of Pb in tomatoes 0.39±0.1 mg/kg he values obtained are similar to the value 0.26 – 0.70 mg/ kg by Mahmood and Malik. Pb in tomato showed concentrations above maximum permissible limit and standard value. Nassar, 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 [58]. Al-Jaboobi et al. reported higher concentration of 10. 75 mg/kg in wastewater irrigated tomatoes [59].

The mean concentration of Arsenic in tomatoes was 0.22±0.03 mg/kg. This concentration is high compared to 0.06±0.02 mg/kg [44] and lower than 0.62±0.19 mg/kg findings by Duressa and Leta [60]. The high value of Arsenic in Jos might be due the closeness of the mining pond to leather/tannin Company who equally uses the water and also discharges its influents close to the pond. The mean of Cr were also high in the study areas, 0.13±0.01 mg/kg seasons. The high value of Cr obtained in this study is lower compared to 0.66 mg/kg reported by Orish et al [61] and 2.97 mg/kg by Yadav et al. [62], in a similar mining sites. Cd was a little high in some site this might have been due washing by runoff water from the immediate vicinity since several anthropogenic processes took place and are still occurring in small scale by illegal miners. This is agree with the 0.12 mg/L reported by Saglam [63] on the study of vegetables in dry – and – season in Southern Turkey. The high concentrations of some of these metals in the areas could be as a result of the closeness of the mining ponds to major traffic highways The order of metal concentration in tomatoes in this work is; Mn > Zn > Pb > Cu > Cr > As > Cd. Heavy metal accumulation in tomato due to long-term wastewater irrigation was also highlighted by Sharma [64].

Garden egg

The mean concentrations of each heavy metals for garden egg in the three sites shows that Pb (0.40), Cr (0.13) and Mn (0.83) mg/kg were higher than the standard permissible limit FAO/WHO in both study sites. The order of heavy metals accumulation in garden egg was Zn > Pb > Mn > Cr > Cu > As > Cd. Pearson's correlation shows that in garden egg Pb is positively correlated with As, while Cu is positively correlated with Zn, Cr, Fe and negatively correlated with Mn. The results obtained in this study were similar to the reported studies some scholars [66] [65]. Tukura et al., reported high levels of Zn (1.60) and Pb (0.36) mg/kg.

Pepper

The mean concentration of Pb (0.177±0.01), Cr (0.132±0.03), Cd (0.007±0.01) and Mn (0.253±0.03) mg/kg were obtained in this study. All metals show order of concentration Cu > Zn > Mn > Pb > Cr > As > Cd. The concentrations of Mn, Cr, Pb and Cd in pepper have crossed the prescribed safe value of WHO/FAO [67] and EU standard, respectively but within the limit of Indian standard. The high concentration of these metals in pepper might be attributed to high level of pesticides and fertilizer on farmland for better yield of crops. Duressa and Leta, 1.15±0.29 mg/kg accumulation of Cd in pepper. Dorcas et al. (2016); Jolly et al. [68]; also reported high concentration of heavy metals in pepper irrigated with wastewater from mines and industrial discharges to soils.

TABLE 3. MEAN ±SD OF HEAVY METAL CONCENTRATION IN VEGETABLES IRRIGATED TIN MINE WATER (MG/KG)

Metals	Tomato	Garden Egg	Pepper	Cabbage	Carrot	Spinach
Pb	0.392±0.07	0.316±0.01	0.177±0.01	0.271±0.05	0.545±0.03	0.376±0.03
Cu	0.077±0.01	0.085±0.03	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	0.007±0.01	0.011±0.01	0.013±0.10	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
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

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Cabbage

The mean concentration of Pb in cabbage from the study sites was 0.27±0.05 mg/Kg while, Cd, As and Cr were 0.011±0.01, 0.043±0.04 and 0.089±0.03mg/kg, respectively. Cd was also slightly high with range of though lower than 0.22±0.2 mg/kg reported by Benti [69], 1.61±0.2 mg/kg by Abdul et al. [70] and 6.25±1.2 mg/kg Kumar and Seema [71]. Similar studies conducted and show the same trend of metal behavior in cabbage [58]. The order of concentration of the heavy metals in dry – and – rainy seasons is Pb > Zn > Mn > Cr > Cu > As > Cd.

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 [72]. This also agrees with the fact 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 [73].

Carrot

The mean of heavy metals in the carrot analyzed from the sites studied showed that the concentrations are higher in all the field except for metals Cu and Zn. All studied metals crossed the safe limit of FAO/WHO standards and EU 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 0.013–0.915 mg/kg with Mn having a high concentration of 0.682±0.04 mg/kg. The studied metals are in descending order of Zn > Mn > Pb > As > Cr > Cu > Cd. Dorcas et al., showed that cadmium (Cd) had mean concentration of 0.36 mg/kg in carrots higher than 0.13 mg/kg recorded in this work[57]. Higher values of these metals were also reported by Mafuyai et al., in his studies on mining pond water in Bokkos, Nigeria [23].

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 Pb has mean concentration of 0.399 mg/kg, while Cr has (0.115±0.00), Mn (0.162±0.01), Cd 0.005±0.00 and As (0.055±0.01 mg/kg. Comparing with the prescribed standards it is found that Pb, Cr, As, Mn and Cd concentrations in spinach crossed the safe limit of WHO/FAO and EU However, the major sources of this contamination may be due to the mining pond water used in irrigation, solid waste disposal, sludge applications, vehicular exhaust and agrochemicals. 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 [74]. 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 [75].

The tin mining pond water used for irrigation purposes may route the uptake of heavy metals from roots to the edible parts of the vegetables. Industrial and traffic emission, burning of fossil fuel, discharge of Pb^{2+} storage batteries, sewage water, and paints/pigment may be the main sources of Pb2+ while Cr2+ is discharged from electroplating and pigments/paints industries, textile mills and tanneries in the city of Jos. In human body Cd2+ induces the gastrointestinal problem and severe toxic effects on different body parts like the kidney, liver, ovaries, testis, nervous system and cardiovascular system.

D. Transfer efficiency (TF) of heavy metals from soil to vegetables

Transfer efficiency or transfer factor (TF) is an index used to assess the mobility of metal from soil to plant which is one of the key components of human exposure to metals through the food chain. The TF values of Pb, Cu, Cd, Zn, Cr, Mn and As for various vegetables vary greatly and the transfer factor of different heavy metals in cultivated vegetables in respect with irrigated soil and vegetables showed that Cd was highest in all vegetables studied with Zn in Pepper. Table 4 summarizes the transfer efficiency of heavy metals in vegetables from the study area. The values of transfer factor ranged from Pb (0.005 – 0.011), Cu (0.005 – 0.023), Cd (0.010 – 0.084), Zn (0.02 – 0.041), Cr (0.007 – 0.024), Mn (0.011 – 0.058) and As (0.00 – 0.001).Among the tin mining pond water irrigated fields' vegetables, maximum TFCd (0.084) found in spinach and the lowest in TFCr (0.018). The rank of transfer factor the heavy metals in vegetables appeared as TF:

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

TABLE 4. TRANSFER FACTOR OF HEAVY METALS FROM SOIL TO VEGETABLES GROWN

Metals	Tomatoes	Garden Egg	Pepper	Cabbage	Carrot	Spinach
TF_{Pb}	0.005	0.010	0.006	0.011	0.007	0.001
TF_{Cu}	0.005	0.023	0.015	0.021	0.011	0.017
TF_{Cd}	0.036	0.027	0.067	0.010	0.056	0.084
TF_{Zn}	0.020	0.037	0.021	0.041	0.041	0.029
TF_{Cr}	0.018	0.024	0.011	0.007	0.013	0.015
TF_{Mn}	0.011	0.014	0.015	0.022	0.022	0.058
TF_{As}	0.007	BDL	BDL	BDL	0.002	BDL

But all the transfer factor values are <1, which indicates the vegetables are exclude from the uptake of heavy metals. The transfer factor in of heavy metals in each of the vegetable studied is the trend of:

Tamatoes: Cd >Zn>Cr > Mn > As > Pb = As,
Garden Egg:Zn >Cd >Cr>Cu >Mn > Pb > As,
Pepper: Cd > Zn > Mn = Cu > Cr > Pb > As,
Cabbage:Zn > Mn> Cu > Pb > Cd > Cr > As,
Carrot: Cd > Zn > Mn > Cr > Cu > Pb >As
Spinach:Cd > Mn > Zn > Cu > Cr > Pb > As.

The transfer factor of irrigated soil to cultivated vegetables also studied by Ibrahim et al. [76] reported the

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TF of the heavy metals from soils to lettuce in his study to be Fe (0.72), Zn (0.71) Cu (0.67), Cd (0.64), Cr (0.43) and Pb (0.42). Tukura et al. in his findings, showed that the potential for metal uptake from soil by vegetable varied in decreasing order of Cd >Zn>Ni > Mn>Cu>Pb [40].

The relative efficiency of plants to accumulate heavy metals in their edible and non-edible parts is influence by pH, bioavailability metals and the transport of heavy metals in the soil. Heavy metals mobility decreases with increase in soil pH due the precipitation of hydroxides, carbonates or the formation of insoluble complexes [77].

E. Daily intake of metals (DIM)

The consumption of vegetables irrigated with tin mining pond water show highest daily intake in Cd in tomato, carrot, spinach and pepper. The highest daily intake of Zn occurs through the consumption of garden egg and cabbage in the study sites (Table 5). The high consumption of Mn was also observed in cabbage and spinach among other vegetables. The estimated daily intake (DIM) of heavy metals from vegetables irrigated with tin mining pond water were in the order:

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

TABLE 5. DAILY INTAKE OF HEAVY METAL (ON DRY WEIGHT BASIS) FOR HEAVY METAL DUE CONSUMPTION OF VEGETABLES

Vegetables	Pb	Cu	Cd	Zn	Cr	Mn	As
Tomato	0.00020	4E-05	1E-05	0.00030	6.87E-05	9.7E-05	0.00011
Garden Egg	0.00020	4.5E-05	3.1E-06	0.00018	5.98E-05	9.8E-05	2.9E-05
Pepper	9.3E-05	0.00023	3.1E-06	0.00022	6.92E-05	0.00013	1.7E-05
Cabbage	0.00014	3.8E-05	5.8E-06	0.00014	4.67E-05	8.8E-05	2.3E-05
Carrot	0.28591	0.81313	0.06820	0.00480	0.00829	0.03578	0.00013
Spinach	0.00020	0.00039	2.62E-04	0.00029	6.03E-05	8.5E-05	2.6E-05

From the values of DIM of metals it is quite clear that among consumer of the cultivated vegetables in the study areas are unsafe as heavy metals bioaccumalate in a biota. The daily heavy metal intake through vegetable consumption in this study is less than RfD limits; for Pb (0.0035), Mn (0.033), Cr (1.5), Cd (0.001), Zn (0.30), Cu (0.04), Fe (0.700) and As (0.0003) mg/Kg. day, respectively set by the US EPA, Integrated Risk Information System (IRIS) which will not poses human health problem. All DIM values of metals showed significant difference in all metals. Similar kinds of finding were observed [61] on metal concentrations increased in the order Ni > Zn > Cu > Cr > Se > Cd and ranged from 0.89-74.02 mg/kg. The values of DIM in this study are collaborated with the findings of DIM for Cu, Ni, Cd, Cr, Pb and Zn ranged from 1.8x10-3 - 7.5x10-3, 8.1x10-4 - 2.5x10-3, 4.9x10-5- 1.4x10-4, 1.4x10-4- 1.2x10-3, 1.1x10-3 - 2.8x10-3 and 6.7x10-3 - 1.4x10-2 mg/kg /day, respectively, [50] for Trend of the metal intake by all vegetables are: Zn > Cu > Pb > Ni > Cr > Cd. Trend of health risk of heavy metals for the consumption of vegetables are Pb > Cu > Cd > Ni > Zn > Cr.

F. Health risk index (HRI)

Table 6 summarizes the health risk indexes of heavy metals in vegetables from the study area. It ranges from The HRI values of Pb were higher in tomato, garden egg, carrot and spinach. As was high in garden egg and cabbage, while other metals show negligible HRI in the vegetables grown in both fields under consideration of health risk. The HRI values of Cd (2.293) in carrot and As (0.979) in garden egg consumed were highest in the vegetables which have the likelihood of posing substantial HRI. The HRI in terms of the vegetables and heavy metals in the studied vegetables is in order:

Carrot > Garden Egg > Tomatoes > Cabbage > Pepper > Spinach and Cd > As > Pb > Mn > Cu >Zn > Cr

TABLE 6. HEALTH RISK INDEX FOR HEAVY METAL DUE TO CONSUMPTION OF VEGETABLES

Vegetables	Pb	Cu	Cd	Zn	Cr	Mn	As
Tomato	0.8714	0.0010	0.0100	0.0010	0.0000	0.0241	0.376
Garden Egg	0.7571	0.0011	0.0031	0.0006	0.0000	0.0244	0.979
Pepper	0.2653	0.0058	0.0031	0.0007	0.0000	0.0332	0.560
Cabbage	0.0406	0.0010	0.0058	0.0005	0.0000	0.0220	0.756
Carrot	0.5169	0.0020	2.2930	0.0016	0.0001	0.0894	0.428
Spinach	0.0564	0.0098	0.0026	0.0010	0.0000	0.0212	0.087

All HRI values of metals showed significant difference in all metals except Cr. Orish et al. also show the HRI values of heavy metals for adults from vegetable consumption to be in this decreasing order Ni > Cu > Zn > Cd > Se > Cr [61]. Kumar and Seema reported the human health risk index calculated for metals of vegetables for adult and its rank appeared as Pb > Cd > Mn > Ni > Cu > Cr in case of vegetable grown with sewage water at all locations [71]. The trend of HRI for vegetables grown at the locations was in the order Cd > Mn > Ni > Pb > Cu > Cr. The findings of this study regarding DIM and HRI suggest that the consumption of vegetables grown in well water and mining pond water irrigated soils is nearly free of risks while others are at the risk of the local population (all the HRI values are less than (1) except Cd in Carrot), but bioaccumulation of this metals can be detrimental as there are also other sources of heavy metal exposures such as dust inhalation, dermal contact and ingestion (for children) of metal-contaminated soils, which were not included in this study [78].

IV. Conclusion

The continuous tin mining pond water irrigation has changed the soil physicochemical characteristics and has led to heavy metal uptake by food crop, predominantly vegetables. The present study revealed that tin mining pond water irrigated soil and food crops grown at the agricultural field were moderately enriched with Pb, Cd, Mn, As, and Cr. In vegetables the extent of heavy metals enrichment was in the order of Cd > Mn > Zn > Cr > Cu > As > Pb. The transfer factor values were <1, which indicates the vegetables are exclude from the uptake of heavy metals. The daily heavy metal intake through vegetable consumption in this study is less than RfD limits. Though, the values of DIM of metals were less it is evident that consumer of the cultivated vegetables in the study areas are unsafe as heavy metals bioaccumalate in a biota. The research also revealed that vegetables have a higher capability to accumulate the heavy metals from soil. The HRI indicated that vegetables grown with tin mining pond water are free from any risk; however, carrot and garden egg pose a serious health risk, particularly with Cd^{2+} and AS^{2+}. Therefore, long-term use of tin mining pond water for irrigation purpose may lead to the severe risk to consumer's health. It is paramount that urgent attention is required for the implementation of proper means to monitor and regulate the industrial and municipal effluents.

V. Recommendations

Taking the health risks in diet as a result of high level of heavy metals in vegetables, the maximum allowable levels of these metals in vegetables should not exceed levels that reflect good agriculture practices. Farmers should be educated on the problems associated with excessive usage of fertilizers and other chemicals, as well as irrigating the vegetables with waste water and the need to grow vegetables with safe levels of heavy metals. The data generated must be used as baseline wastewater quality framework to serve as a basis for monitoring irrigation water quality in urban areas of Rewa to ensure safety.

The high HQ of Pb suggested that the consumption of Spinach grown in waste water irrigated site of Naubasta is not free of risks. Responsible agencies should carry out public health education within the consumption area to sensitive the general public on the potential effects of indiscriminate disposal of waste and the potential health hazards associated with the consumption of vegetables cultivated with wastewater. Measures must be taken to reduce heavy metal pollution and nutrient loading of irrigation water and soils to protect the safety of both farmers and consumers.

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