HEAVY METAL CONCENTRATION IN SOIL IRRIGATED WITH EX- TIN MINING PONDS WATER, BOKKOS L.G.A PLATEAU STATE, NIGERIA

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ABSTRACT: *Metal contamination issues are becoming increasingly common in Nigeria and elsewhere, with many documented cases of metal toxicity in mining industries, foundries, smelters, coal-burning power plants and agriculture. The purpose of this study is to analyse for the concentration of selected heavy metal (Pb, Cu, Cd, Zn, Cr, Fe, Mn and As) of the soils on which the crops were grown, using atomic absorption spectrometry (AAS). The following concentrations (mg/Kg) of the metals were found in the soil samples irrigated with tin mining pond water: Pb (45.4 – 58.9), Cu (20.0 – 28.5), Cd (0.77 – 1.21), Zn (35.7 – 53.5), Cr (17.9 – 22.9), Fe (507 – 618), Mn (35.7 – 48.0) and As (68.3 – 137) and in rainy season: Pb (40.2 – 47.3), Cu (21.7 – 29.2), Cd (0.55 – 1.13), Zn (26.5 – 39.3), Cr (5.32 – 9.65), Fe (563 - 584), Mn (52.0 – 71.4) and As (47.5-129). The general trend of the geoaccumulation of metals in both dry and – rainy season is Cd > Cr > Pb > Zn > As > Cu > Fe > Mn and Cd > Pb > Cr > Zn > Cu > Mn > Fe > As, respectively. Soils collected during dry season from the study sites shows sequence of enrichment in descending order as Cd > Cr > Cu > Pb > Fe > Zn > As >Mn and Cd > Zn > As > Pb > Cu > Fe > Cr > Mn, The study revealed that tin mining pond water increases the concentration of metals in the soil which are subsequently absorbed by the plants.*

KEYWORDS: Heavy Metals, Tin Mining, Accumulation, Soil Contamination, Nigeria

INTRODUCTION

The mining industry is one of the oldest in the world, and its importance to human development becomes evident when one considers the naming of the pre-historic age after mined products "Stone" age, "Bronze" age and "Iron" age (Jennings, 1999). Mining on the whole is the extraction of valuable mineral resources or other geologic materials from the earth, usually from an ore body, vein or seam (Encarta Encyclopedia, 2001). Over the years, mining evolved all over the world to include various minerals such as the mining of malachite at Maadi by ancient Egyptians, gold and iron at Wales by the Romans and turquoise in pre-Columbian America (Onwuka *et al.* 2013).

In Nigeria, mining started as far back as the eighteenth century. Over five hundred (500) occurrences and deposits of different minerals are known so far to exist within the country with the exploration of some of them being on a small scale (Adegbulugbe, 2007). One of the major cases of mineral exploration and exploitation that boomed within the nation has been that of tin in Plateau State North Central Nigeria.

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 (Adegbulugbe, 2007). 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 (Ajaegbu, *et al*, 1992). 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.

Mining involves a variety of operations which can be environmentally disruptive if proper siting, design, construction, operation and follow-up monitoring are not provided (Abua and Eyo, 2013). According to Vincent *et al.* (2012) the operations are known to have various negative effects on our environment such as alteration of landscape, deterioration of vast land areas, extinction of wild life, etc. Larger (2014) also reported that mining activities are also associated with dust particles which constitute one of the most invasive and potentially irritating air pollutants. The dust generated reduces visibility which poses a potent threat to both human health and the environment. The impact of dust generated during mining is influenced by several site conditions including rock properties, size of the mining operation, proximity to population centres and other nearby sources of dust, moisture, ambient air quality, air currents and prevailing winds (Okorie et al., 2012).

Metal contamination in abandoned mines is a global environmental problem which various countries around the world are suffering from. This problem ranks among the most significant environmental challenges worldwide, which requires ongoing evaluation and urgent solution to overcoming this problem and its negative impacts (Kutty and Al-Mahaqeri, 2016)

Open cast mining gives rise to large number of excavated overburdens dumped on the surface (mine spoil); this may contain various heavy metals, some of which are toxic in nature and affect the environment when their concentration exceeds the permissible limit. 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 that may lead to geo-accumulation and subsequent bio-accumulation and bio-magnifications in the food chain (Koushik *et al***.,** 2012). Uncontrolled mining activities and illegal mining in developing countries have generated a lot of environmental hazards and enormous amount of wastes and different types of pollutants generated (Onyedika and Nwosu, 2008; Atafar *et al*, 2010). These caused heavy metals to get accumulated through time in soils and plants thereby creating a negative influence on physiological activities of plant growth, dry matter accumulation and yield (Ojekunle, 2014). In some cases, tailings present on steep slopes are unstable and prone to erosions. All these factors contribute to pollution for the soil, ground and surface water. Metals are non-degradable and therefore can persist for long period in aquatic as well as terrestrial environments (Nouri *et al.,* 2012). These metals may be transported through soils to reach ground water or may be taken up by plants including agricultural crops (Atafar *et al.,* 2010). 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.

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 soil, sediment and water, thus causing metal contamination in water bodies. 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 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).

The people of these areas are predominantly farmers and hunters due to the topography of the area; they are commonly engaged in the cultivation of vegetables such as: tomato, pepper, cabbage, carrot, spinach, garden egg and many other varieties of vegetables. These mining pond waters are used for irrigating the vegetable farmlands and many other varieties of crops, and also serve as major source of drinking water and for domestic activities. The soil is an important media that plays a vital role in the development plants and mankind, hence the need to seek the possible connections between the concentrations of heavy metals in the soil.

MATERIALS AND METHODS

Study Area

The study was carried out in Bokkos Local Government Area of Plateau State as shown in (Figure 1). The study areas lie between latitude 9°28'00.00''N to 9°24'40.00''N and longitude 8°54'00.00''E to 8°56'.00''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.

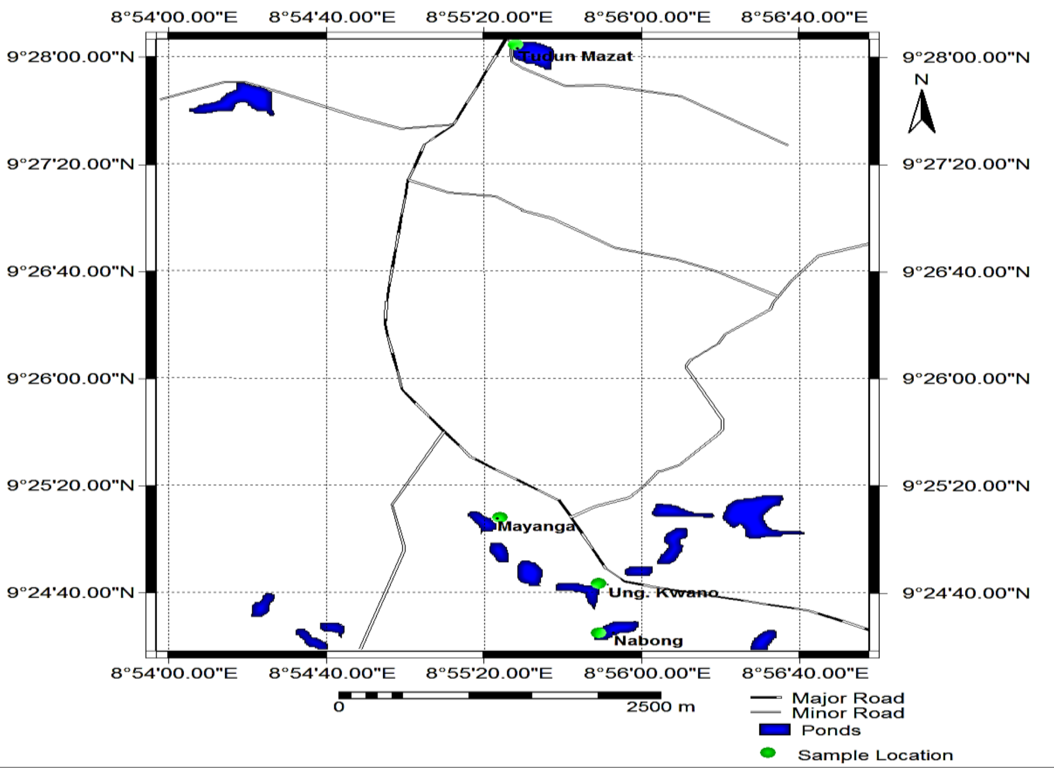

Figure 1: Map of Bokkos Showing Study Areas

Soil Sampling and Preparation

Soil samples were obtained from two farms each irrigated with the pond water in the various Local government areas. The soil samples were 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. About 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 (Hseu *et al.*, 2002). The concentrations of Pb, Cr, Cu, Cd, Zn, Mn and As were be determined by Atomic Absorption Spectrophotometer PG (FAAS. PG990) (Mafuyai *et al.*, 2015).

Geoaccumulation index (Igeo)

The index of geoaccumulation (Igeo) is widely used in the assessment of contamination by comparing the levels of heavy metals obtained to background levels originally used with bottom sediments (Atiemo et al., 2011; Muller, 1969). It is calculated using the equation:

where, C_n represents the measured concentration of the elements studied and Bn is the geochemical background value of the element in fossil argillaceous sediment (average shale). The following classification is given for geoaccumulation index: (Lu *et al.*, 2009)

$$\text{Igeo} = \log_2^{\left(\frac{C_n}{1.5B_n}\right)} \quad (1)$$

Table 1. Geoaccumulation index (Igeo) Classification

Igeo	Degree of Pollution
<0	Practically Unpolluted
0–1	Unpolluted to Moderately Polluted
1–2	Moderately Polluted
2–3	Moderately to Strongly Polluted
3–4	Strongly Polluted
4–5	Strongly to Extremely Polluted
> 5	Extremely Polluted

Pollution Load Index

Pollution load index (PLI) for each site was evaluated using the formula:

$$PLI = (CF_1 \times CF_2 \times CF_3 \times \ldots\ldots\ CFn\ )^{1/n} \quad (2)$$

where: n = number of metals

CF = contamination factor.

PLI is a potent tool in heavy metal pollution evaluation. According to Chakravarty and Patgiri (2009), the PLI value higher than 1 indicates the samples have be polluted while the PLI value less than 1 indicates no pollution occurred.

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:

$$CF = \frac{C_{metal}}{C_{background}} \quad (3)$$

where: C_{Metal} is the concentration of a given metal in the soil

$C_{Background}$ is a metal concentration of a control soil sample.

The CF value for describing the contamination levels is summarized in Table 2.

Table 3: 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

Statistical Analysis

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

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

$$r = \sum \frac{(\overline{X} - X)(\overline{Y} - Y)}{nSxSy} \qquad (4)$$

where, r = coefficient of correlation,

X = variable X,

$\overline{X}$ = mean of variable X,

Y = variable Y,

$\overline{Y}$ = mean of variable Y,

n = number of pairs of variables,

Sx= SD of variable X,

Sy = SD of variable Y.

Figure 2: An Abandoned Dragline used in Tin Mining

Figure 3: Abandoned Tin Mining Pond at Angwan Kwano use for Irrigation

RESULTS AND DISCUSSIONS

The study was conducted to investigate concentration of heavy metals in soil and vegetables due to ex- tin mining pond water to estimate their possible concentrations. Soil and vegetables samples from four tin mining sites of Bokkos Local Government Area were analyzed and studied for the concentrations of Pb, Cu, Cd, Zn, Cr, Fe, Mn and As as shown in (Tables 3 – 6) below.

Table 3: Mean Heavy Metals Concentration in Soil Irrigated with Mining Pond Water (mg/Kg)

Soil	Pb	Cu	Cd	Zn	Cr	Fe	Mn	As
A_1	45.3	24.7	1.50	40.5	22.7	595	40.8	68.3
A_2	58.0	28.2	1.01	35.2	18.7	618	40.1	90.5
A_3	54.0	20.0	0.78	47.9	18.3	507	47.4	135
A_4	57.8	26.8	0.19	53.4	17.6	532	35.7	137
Mean	53.8	24.9	0.88	46.4	19.33	563	41.0	108

SE	3.18	2.05	0.08	4.55	1.28	27.8	3.08	17.2
SD	5.15	3.10	0.47	6.95	1.99	45.1	4.18	29.4
Range	12.7	8.2	0.31	17.8	5.10	111	11.7	68.7
Min	45.4	20.0	0.77	35.7	17.9	507	35.7	68.3
Max	58.9	28.5	1.21	53.5	22.9	618	48.0	137

Ponds: A_1 =Nabong, A_2 = Agwan - Kwano, A_3 = Maiyanga, A_4 = Tudun – Mazat,

Table 4: Pearson's Correlation Coefficient Matrix of Mean Heavy Metals in Soil Irrigated Mining Water

	Pb	Cu	Cd	Zn	Cr	Fe	Mn	As
Pb	**1.00**							
Cu	**0.35**	**1.00**						
Cd	**-0.77**	**-0.09**	**1.00**					
Zn	**0.22**	**-0.34**	**-0.78**	**1.00**				
Cr	**-0.94**	**-0.04**	**0.88**	**-0.48**	**1.00**			
Fe	-0.19	0.70	**0.64**	**-0.88**	**0.51**	**1.00**		
Mn	**-0.26**	**-0.85**	**0.35**	**-0.14**	**0.07**	**-0.33**	**1.00**	
As	**0.64**	**-0.35**	**-0.90**	**0.82**	**-0.86**	-0.88	**0.09**	**1.00**

Table 5: Mean Heavy Metals Concentration of Soil (mg/Kg) Cultivated in Rainy Season

Soil	Pb	Cu	Cd	Zn	Cr	Fe	Mn	As
A_1	40.2	23.4	1.13	37.1	5.32	577	57.5	47.5
A_2	44.2	29.2	1.04	39.3	8.44	584	53.8	87.2
A_3	45.2	21.7	0.73	26.5	9.65	568	71.4	129
A_4	47.3	22.3	0.55	38.5	9.13	563	52.0	123
Mean	44.2	24.1	0.86	35.3	8.14	573	58.7	96.6
SE	1.78	1.88	0.15	3.19	1.08	5.25	4.85	20.4
SD	2.58	2.98	0.23	5.17	1.68	8.09	7.61	32.6
Range	7.10	7.50	0.58	12.8	4.33	21.0	19.4	81.5
Min	40.2	21.7	0.55	26.5	5.32	563	52.0	47.5
Max	47.3	29.2	1.13	39.3	9.65	584	71.4	129

Ponds: A_1 =Nabong, A_2 = Agwan - Kwano, A_3 = Maiyanga, A_4 = Tudun – Mazat,

Table 6: Pearson's Correlation Coefficient Matrix of Mean Heavy Metals in Soil During Rainy Season

	Pb	Cu	Cd	Zn	Cr	Fe	Mn	As
Pb	**1.00**							
Cu	**-0.17**	**1.00**						
Cd	**-0.90**	**0.57**	**1.00**					
Zn	-0.11	**0.56**	**0.28**	**1.00**				
Cr	0.91	**-0.09**	**-0.77**	**-0.40**	**1.00**			
Fe	**-0.62**	**0.86**	**0.90**	**0.38**	**-0.47**	**1.00**		
Mn	**-0.04**	**-0.47**	**-0.11**	**-0.98**	**0.28**	**-0.22**	**1.00**	
As	**0.92**	**-0.36**	**-0.90**	**-0.48**	**0.96**	**-0.69**	**0.34**	**1.00**

Lead (Pb)

The concentration of Pb in the soil samples irrigated with tin mining pond water collected from both farms showed little higher value in treated soil than in rainy season soil. The Pb concentration ranged from 45.3 – 58.0mg/Kg and 40.2 – 47.3 mg/Kg with a mean of 53.8±5.15 and 44.2 ±2.58mg/Kg concentration in the soil irrigated with tin mining pond water and the rainy season (Tables 1 and 2), respectively. The result shows high concentration of heavy metals in the soil irrigated with tin mining pond water. The values of lead in the soil irrespective of season and farm soil are within the prescribed safe limit of irrigation soil FAO/WHO, 2008 standard limits. The value of Pb obtained is in agreement with that 46.75 mg/Kg reported by Daniel *et al.*, (2014) in Kassa Ropp Barkin-Ladi and Deribachew *et al.* (2015). Similar work done by Mahmood (2016) revealed Pb content in soil to range from 12 – 58.2 mg/Kg, while Lenka and Danica, (2014) shows a range of 14.0 – 102 mg/Kg higher than the current study. Chaoua *et al*. (2018) reported the concentration of Pb as 57.36mg/Kg in soil irrigated with wastewater in the region of Marrakech in Morocco.

From the correlation it is found that soil treated with mining pond water, Pb is positively correlated with As and negatively correlated with Cd in both seasons, but a significant positive correlation is shown between Pb and Cr in soil collected during rainy season (Annexure 1 and 2). The study also showed the significant difference ($p < 0.05$) in the Pb content of the rainy season soil and treated soils collected in both seasons. The Pb enrichment in the mining pond water irrigated soils as compared to rainy season soil are corroborated with the findings of Mahmood and Malik (2014); Lente *et al.*, (2012).

Copper (Cu)

The mean value of Cu in mining pond water treated soil (Figure 1 and 2) collected from various soil irrigated tin mining pond water was in the ranged of 20.0 – 28.2 and 21.7 – 29.2 mg/Kg with mean of 24.9 ±3.10 and 24.1 ±2.98 mg/Kg in the irrigated soil during dry - and - rainy season respectively. Comparing the result obtained in this study the value is higher than the reported value of 17.7 mg/Kg by Chaoua *et al.* (2018) but however, lower than the reported concentration range of 42.01 – 111.6 mg/Kg and 28.9 – 57.1 mg/Kg of Kabir *et al.* (2017) and Minhaz *et al.* (2019) which recorded extremely high concentrations of copper at industrial sites beyond the acceptable agricultural soils limits of 50 mg/kg. It is observed that there is accumulation of Cu in the soil as a result of anthropogenic and industrial processes. The Cu level in the irrigated soils is within the safe limit for cultivation. The study also showed the significant difference ($p < 0.05$) in the Cu content of rainy season and treated soils collected in both seasons. The metals contents in both types of irrigation water soil and rainy season soil corroborated with the findings of Henry *et al.* 2018 and Singh *et al.* 2010**.**

Cadmium (Cd)

The concentration of Cd in the mining pond water treated soil and rainy season soil in both study sites shows a range of 0.19 – 1.50 and 0.55 – 1.13 mg/Kg having a mean of 0.88 ±0.47 and 0.86 ±0.23 (Figures 1 and 2). The value obtained in this work is in agreement with Deribachew *et al.* (2015) and lower compared to 3.51mg/Kg reported by Daniel *et al*. (2014) in Barkin – Ladi Plateau State and 12.62 – 20.7 mg/Kg by Kabir *et al.* 2017 in contaminated soil. Comparing with the safe limit of Cd in the soil it is found that, both treated and rainy season soil are within the prescribed standards of 3 – 6mg/Kg set by Indian Awashti (2000) and USEPA, (2010). Cadmium concentration in soil is relatively high, this may be attributed to applications of fertilizers and other farming practices including used of pesticides (Peter *et al.* 2014). 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 study also showed the significant difference ($p < 0.05$) that Cd is positively correlated with Cr and As in the soil irrigated with mining pond water and negatively correlated in soil collected during rainy seasons. In this study Cd content in both irrigated soils are corroborated with the study of (Deribachew *et al.* 2015; Mahmood and Malik, 2014; Daniel *et al.* 2014 Ghosh *et al.* 2012 and Gupta *et al*. 2010).

Zinc (Zn)

The mean concentration of Zn in the tin mining pond water treated soil and rainy season shows that it ranged from 35.2 – 53.4 and 26.5 – 39.3 mg/ Kg with a mean of 46.4 ±6.95 and 35.4 ±5.17mg/Kg (Figure 1 and 2), respectively. The result of Zn obtained in soil irrigated with the tin mining pond water shows clearly that the water has potential for the development of Zn enrichment. The Zn content in both studied soils is within the safe limit of prescribed standards USEPA, (2010). The Zn concentration in the mining pond water irrigated soil as compared with rainy season soil also corroborated with the previous studies of Tukura *et al* 2016; Mahmood and Malik, 2014; Lente *et al*., 2012 and Sinha *et al.*, 2006.

Chromium (Cr)

The soil samples that were collected during dry – and – rainy season exhibits a range of 17.6 – 22.7 and 5.32 – 9.65 with the mean Cr content in mining pond water treated soil as 19.31 ±1.99mg/Kg and 8.14 ±1.68mg/Kg in rainy season. It was observed that Cr in soil irrigated with tin mining pond water doubled more than two times higher than rainy season soil (Figure 1 and 2). The concentration obtained even though high, is lower than the value 54.17mg/Kg reported by Daniel *et al.*, 2014 in Kassa Ropp for similar tin mining soil. However, the low value in rainy season may be as a result of heavy rains which leached Cr metal beneath the soil. The Cr concentration in soil irrespective of treatment are within the safe limit of EU, (2002) standard. (Tables 1 and 2). Cr in this study is positively correlated with As in rainy season soil and negatively correlated in soil irrigated with mining pond water. Chromium enrichment in the mining water irrigated soils as compared with rainy water soils as corroborated with the findings of Mahmood and Malik, 2014; Ghosh *et al.*, 2012; Gupta *et al.*, 2010 and Sinha *et al.*, 2006.

Iron

The soil sample irrigated with mining pond water during dry season at the various sampling sites gave a range of 507 – 618 mg/Kg and rainy season 563 – 589 mg/Kg with the mean concentration as 563.03 ±45.1 mg/Kg, and 573.05 ± 8.09mg/Kg, respectively. The higher concentration of Fe observed in the soil around mining ponds, might be as a result of the washing of mining piled dumps by runoff water during rainfalls. The results show that iron (Fe) is the most abundant essential metal in both soil and 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 the surfaces. Similar work reported higher values of Fe as reported in this work (Boamponisem *et al.*, 2012). However, the value Fe in both soil sample were above WHO permissible limit.

Manganese (Mn)

The soil irrigated with mining pond water during dry season showed mean concentration of 41.0 ±4.18 mg/Kg with a range of 35.7 – 47.4 mg/ Kg and 58.7±7.61mg /Kg in soil collected during rainy season with a range 52. 0 – 71.4 mg/Kg higher than soil irrigated with tin mining pond water. The value obtained from both study soils is lower compared to 80.0 mg/Kg Mn soil quality standards USEPA (2010). The lower Mn content in the tin mining pond water irrigated soils as compared with rainy season irrigated soils corroborated with the findings of (Mahmood and Malik, 2014 and Gupta *et al*., 2010). As low level of manganese intake is essential for human health but exposure to high level of manganese are toxic. Inhaled manganese is directly transported to brain before metabolized to liver. Permanent neurological disorder known as magnetism is a result of manganese toxicity and symptoms of that is tremors, difficulty walking and facial muscle spasms. High level of manganese inhalation can cause series of serious and disabling neurological effects in humans

Arsenic

The mean concentration of As in mining pond water treated soil (Figure 3 and 5) and rainy seasons soil from the sites are 108 ±29.4 and 96.6 ±32.6mg/Kg, respectively. The values ranged from 68.3 – 137mg/Kg in dry season irrigated tin mining water soil and rainy season farm soil 47.5 – 129 mg/Kg. The values compared to rainy season shows that there is accumulation of As in the soil, this might have been 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. Naturally, elevated levels of arsenic in soils may be associated with geological substrata such as sulfide ores. Anthropogenically contaminated soils can have concentrations of arsenic up to several percent (Porter and Peterson, 1977). Arsenic concentrations of up to 27 000 mg/kg were reported in soils contaminated with mine or smelter wastes (US EPA, 1982). 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 (Takamatsu *et al.* 1982; Sanok *et al.* 1995).

Index of Geoaccumulation

The results of Igeo analysis for both dry – and –rainy season are shown in (Tables5). The degree of metal pollution assessed in terms of seven contamination classes based on the increase numerical value of index shows that, the soil was moderately polluted with Cd and Cr mean of 1.08 and 1.00 in dry season respectively, while Cd with mean 1.53 shows moderate pollution in rainy season. Other metals Pb, Cu, Zn, Fe, Mn and As, practically show no contamination. The general trend of the geoaccumulation of metals in both dry and – rainy season is Cd > Cr > Pb > Zn > As > Cu > Fe > Mn and Cd > Pb > Cr > Zn > Cu > Mn > Fe > As, respectively.

Table 7: Index of Geoaccumulation

Metal	DRY SEASON	RAINY SEASON
	BKK	BKK
Pb	-0.13±0.04	0.22±0.10
Cu	0.36±0.06	0.65±0.05
Cd	1.08±0.13	1.53±0.13
Zn	-0.38±0.05	-0.59±0.07
Cr	1.00±0.04	-0.02±0.10
Fe	-0.27±0.04	-0.13±0.10
Mn	-1.27±0.05	-0.23±0.05
As	-0.71±0.13	-0.79±0.17

In all Cd showed the dominant geoaccumulation in both studied seasons. This might have been attributed to Cd battery from waste dumps along the study area.

Contamination factor (CF) of heavy metals in soil

Contamination factor (CF) of heavy metals in the soil is calculated with help of the formula provided by Kisku *et al.* (2000). Soils collected from the cultivated soils' shows variation in metal content as shown in table 6.

Table 8: Contamination Factor (CF) of Heavy Metals in Soil

	Rainy Season		Rainy Season	
Metal	Mean	PLI	Mean	PLI
Pb	1.40	1.18	1.32	1.14
Cu	1.86	1.36	1.27	1.13
Cd	2.94	1.68	3.84	1.90
Zn	1.22	1.10	1.37	1.17
Cr	2.68	1.63	1.09	1.03
Fe	1.29	1.13	1.14	1.07
Mn	0.72	0.85	0.99	0.99
As	1.04	1.00	1.33	1.15

Soils collected during dry season from the study sites shows sequence of enrichment in descending order as Cd > Cr > Cu > Pb > Fe > Zn > As >Mn and Cd > Zn > As > Pb > Cu > Fe > Cr > Mn, Based on the contamination categories as proposed by Sutherland, (2000) it is found that soils collected during dry season shows slight contamination for Cd (2.94) and Cr (2.68). The rest of the metals suspected to contamination in all seasons except Mn and significant moderate contamination was observed in Cd (3.84) in rainy season. This might be as a result of anthropogenic activities. Higher transfer coefficients reflect high soil contents or greater potentials of plants to absorb metals and bio-accumulate into tissues Abah *et al.* (2012). However, low transfer coefficients have been reported to indicate strong sorption of the metals to soil colloids (Kachenko *et al.*, 2006).

The pollution load index also shows that all soil was susceptible to pollution with all the metals except Mn. Similar trend of pollution is noticed in the order of Cd > Cr > Cu > Pb > Fe > Zn > As >Mn and Cd > Zn > As > Pb > Cu > Fe > Cr > Mn, in dry and – rainy seasons respectively. Contamination factor (CF) of heavy metals in the irrigated soils is also highlighted by Choppra and Pathak, (2012), Kumar and Seema, (2017)

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 dry season. In this study a comparative assessment of Bokkos Local Government Area tin mining pond waters used in irrigation is performed along with the prescribed standards of FAO/WHO, USEPA, EU and India. The soil collected from the irrigated fields shows the improvement of soil heavy metals compared with soil collected from farms during rainy season. Among all studied metals Cd, is found higher as prescribed by European Union Standards, 2002.

The sequence of contamination of heavy metals in soil irrigated with tin mining pond water and rainy season, show same pattern of enrichment and the tin mining pond water irrigation does not pose significant effect on the soil. The contamination of Cd and Cr in the soil compared to other metals studied considering their higher accumulation call for regulatory mechanism. Therefore, regular monitoring of effluents, 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.

REFERENCES

Abah, J., Abdurahaman, F.I., Ndahi, N.P. and Ogugbuaja, V O. (2012). Effects of inorganic fertilizers and herbicides on levels of some heavy metals in soils and grains of rice grown in selected areas of Benue State, Nigeria. *International Journal of Applied and Resources Technology*, **1**: 160-166.

Abua M and Eyo E (2013). Assessment of soils around quarry terrain in Akamkpa local government area, Cross River State-Nigeria. *Merit Research Journal of Agricultural Science and Soil Sciences*, **1**(1):001-005.

Adegbulugbe, A.O (2007). "Issues of Radioactive Waste Arising from Tin Mining Activities on the Jos Plateau" Paper presented to the Nigerian Nuclear Regulatory Authority.

Atafar Z, Mesdaghinia A, Nouri J, Homaee M, Yunesin M, Ahmadimoghaddam, M and Mahvi, A. H. (2010). Effects of fertilizer applicationon soil heavy metal concentration. Environ. Monitor Assess, **I60** (1-4), 83-89.
Awashthi, S.K (2000). Prevention of Food Adulteration Act no. 37 of 1954. Central and State Rules as Amended for 1999, Ashoka Law House, New Delhi.
Boamponsem, G. A., Kumi, M. and Debrah, I. (2012). Heavy metals accumulation in cabbage, lettuce and carrot irrigated with wastewater from Nagodi mining site in Ghana. *International Journal of Scientific and Technology Research*, **1**(11):124-129.
Chaoua, S, Boussaa S, EL Gharmali A and Boumenzzoug A (2018). Impact of irrigation with wastewater on accumulation of heavy metals in soil and crops in the region of Marrakech in Morocco. Journal of the Saudi Society of Agricultural Sciences https://doi.org/10.1016/j.jssas.2018.02.003
Chopra, A. K. and Pathak, C. (2012). Bioaccumulation and translocation efficiency of heavy metals in vegetables grown on long-term wastewater irrigated soil near Bindal river, Dehradun. *Agricultural Research*, **1**(2):157-164.
Daniel, V. N., Chudusu, E. S., Chup, J. A. and Pius, N. D (2014). Variation of Heavy Metals in Agricultural Soils Irrigated with Tin Water in Heipang District of Barkin Ladi, Plateau State, Nigeria. *International Journal of Science and Technology,* **3**(5):674-683.
Daniel, V. N., Chundusu, E. S. and Chup, J. A.(2014). Heavy Metals Accumulation in Agricultural Soils Irrigated with Tin - Mine Water in B/Ladi, Plateau State, Nigeria. *International Journal of Engineering & Technology*, **14**(4): 69 –74.
Deribachew B, Amde M, Nigussie-Dechassa R and Taddesse A.M (2015). Selected heavy metals in some vegetables produced through wastewater irrigation and their toxicological implications in eastern Ethiopia. Journal Toxicology Environmental and Health Science 1001310032.
European Union (EU). (2002). Heavy Metals in Wastes, European Commission on Environment (*http://ec.europa.eu/environment/waste/studies/pdf/heavymetalsreport.pdf)*.
FAO/WHO (2011). Joint FAO/WHO Food Standards Programme Codex Committee on Contaminants in Foods; Fifth Session, 64-89.
FAO/WHO, (2010). Evaluation of certain contaminants in food: seventy-second report of the Joint FAO/WHO Expert Committee on Food Additives (JECFA), WHO Press Geneva, Switzerland.
Ghosh, A. K., Bhatt, M. A. and Agrawal, H. P. (2012). Effect of long-term application of treated sewage water on heavy metal accumulation in vegetables grown in northern India. *Environmental Monitoring and Assessment*, 184:1025-1036.
Gupta, S., Satpati, S., Nayek, S. and Garai, D., (2010). Effect of wastewater irrigation on vegetables in relation to bioaccumulation of heavy metals and biochemical changes. *Environmental Monitoring Assessment*, 165:169-177.
Henry M. U, Ogenyi R. A, Henry U. I and Dogun O (2018). Assessment of Heavy Metal Concentration in Water, Soil and Vegetable in Ex-Mining Pond, Jos South L.G.A Plateau State, Nigeria. International Journal of Scientific and Research Publications, **8**(8): 840 – 845.
Hseu, Z. Y., Chen, Z. S., Tsai, C. C., Tsui, C. C., Cheng, S. F., Liu, C. L. and Lin, H. T. (2002). Digestion Methods for Total Heavy Metals in Sediments and Soils. *Water, Air and Soil Pollution*, 141: 189-205. http://dx.doi.org/10.4236/gep.37002

Jennings, N.S. (1999). “Social and Labour Issues in Small-scale Mines”: Report for Discussion at the Tripartite Meeting on Social and Labour Issues in Small scale Mines. International Labour Office, Geneva.

Kabir A. S, Mohammed S. H, Muazu A. A and Aishatu M. K (2017). Assessment of heavy metals contamination of soil and water around abandoned Pb-Zn mines in Yelu, Alkaleri Local Government Area of Bauchi State, Nigeria international research Journal of Environmental Health, 4(5):72-77.

Kachenko A.G. and Singh B. (2006). Heavy metals contamination in vegetables grown in urban and metal smelter contaminated sites in Australia. Water Air Soil Pollution, 169:101-123.

Kisku, G.C., Barman, S.C. and Bhargava, S.K. (2000). Contamination of soil and plants with potentially toxic elements irrigated with mixed industrial effluent and its impact on the environment. *Water, Air and Soil Pollution*, 120:121-137.

Koushik, S. Kalyan, A and Aniruddha, G (2012). Assessment of Heavy Metal Contamination of Soil In and Around Open Cast Mines of Raniganj Area, India.

Kumar, A., Sharma, I.K., Sharma, A., Varshney, S., Verma, P.S., 2009. Heavy metals contamination of vegetable foodstuffs in Jaipur (India). Electronic Journal of Environmental, Agricultural Food Chemistry **8**(2), 96 -101.

Kutty, A. A and Al-Mahaqeri, S. A. (2016). An Investigation of the Levels and Distribution of Selected Heavy Metals in Sediments and Plant Species within the Vicinity of Ex-Iron Mine in Bukit Besi. Journal of Chemistry. http://dx.doi.org/10.1155/2016/2096147.

Langer, W. H. (2014). Potential Impacts of Quarrying Stone in Karst, a Literature Review. Available at: http://geology.cr.usgs.gov/pub/ofrs/OFR-01-0484/, (accessed 9/02/2014).

Lenka Angelovičová and Danica Fazekašová (2014). Contamination of the Soil and Water Environment by Heavy Metals in the Former Mining Area of Rudňany (Slovakia). Soil and Water Res., **9**(1): 18–24 Original Paper

Lente, I., Keraita, B., Drechsel, P., Ofosu-Anim, J., Brimah, A.K. (2012). Risk assessment of heavy metal contamination on vegetables grown in long-term wastewater irrigated urban farming sites in Accra, Ghana. *Water Quality, Exposure and Health*, B:179 – 186.

Mafuyai, G. M., Kamoh, N. M., Kangpe, N. S., Ayuba, M. S and Eneji, I. S (2015). Heavy Metals Contamination in Roadside Dust along Major Traffic Roads in Jos Metropolitan area, Nigeria. *European Journal of Earth and Environmen*, **2**(1):1-14.

Mahmood A, Malik R. N (2014). Human health risk assessment of heavy metals via consumption of contaminated vegetables collected from different irrigation sources in Lahore, Pakistan. Arabian Journal of Chemistry 7: 91-99.

Minhaz Ahmed, Masaru Matsumoto, Akinori Ozaki, Nguyen Van Thinh and Kiyoshi Kurosawa (2019). Heavy Metal Contamination of Irrigation Water, Soil, and Vegetables and the Difference between Dry and Wet Seasons Near a Multi-Industry Zone in Bangladesh, Water **11** (583)1-12 doi:10.3390/w11030583

Nouri, J., Lorestani,B., Yousefi, N., Khorasuni, N.,Hassani,A. H.,Seif, S., and Cheraghi, M. (2011).Phytoremediation potential of native plants grown in the vicinity of Ahangaran lead-zinc mine.Hamedan Iran. Environ Earth Sci., 62(3), 639-644.

Ojekunle, Z., Adeboje, T.A., Sangowusi, T. A. and Ojekunle, V (2014). Tree Leaves as Bioindicator of Heavy Metal Pollution in Mechanic Village, Ogun State. *Journal of Applied Science and Environmental Management*, 18 (4): 639 – 644.

Okorie A., Entwistle J., and Dean J. R. (2012) Estimation of Daily Intake of Potentially Toxic Elements from Urban Street Dust and the Role of Oral Bioaccessibility Testing. *Chemosphere*. **86**: 460–467.

Onwuka S. U., Duluora J.O and Okoye C.O (2013). Socio-Economic Impacts of Tin Mining in Jos, Plateau State, Nigeria. International Journal of Engineering Science Invention, **2**(7):30-34.

Onyedika, G. O and Nwosu, G. U. (2008). Lead, Zinc and Cadmium in Root Crops from Mineralized Gelena-Sephalerite Mining Areas and Environment. *Pakistan Journal of Nutrition,* 73*:* 418-420.

Paul, B.T, Clement G.Y, Anita, K.P and Dwayne J.S (2014). Heavy Metals Toxicity and the Environment HHS Public Access 10.1007/978-3-7643-8340-46

Peter F, Tengiz F. U, Eliso I. Lars-Christoffer W, Dietrich S, and Besik B. K. (2007). Heavy Metal Pollution of Soils and Food Crops due to Mining Wastes in the Mashavera River Valley. Bulletin of the Georgian National Academy of Sciences, **175(**3)34-42

Sinha, S., Gupta, A.K., Bhatt, K., Pandey, K., Rai, U.N., Singh, K.P. (2006). Distribution of metals in the edible plants grown at Jajmau, Kanpur (India) receiving wastewater irrigated tannery wastewater: relation with physicochemical properties of the soil. *Environmental Monitoring and Assessment*, **115**:1 – 22.

Tukura B. W, Etonihu A.C, Ambo I. A and Iboro (2016). Accumulation of heavy metals in vegetables grown on farmlands irrigated with treated sewage water. FUTN *Trends in Science and Technology Journal.* ***1****(1):168-172*.

USEPA, (2010). Risk-based Concentration Table. United State Environmental Protection Agency, Washington, DC.

Vincent, K. N., Joseph, N. N. and Raphael, K. K (2012). Effects of Quarry Activities on Some Selected Communities in the Lower Manya Krobo District of the Eastern Region of Ghana.

WHO/FAO. (2007). Joint FAO/WHO Food Standard Programme Codex Alimentarius Commission 13th Session. Report of the Thirty-Eight Session of the Codex Committee on Food.