

Original Research Article

The impact of galena mining in north-eastern Nigeria on nearby food crops.

Abstract

Aims: To investigate and evaluate trace elements concentration in soils and bioaccumulation on food crops grown on agricultural fields around galena mine area, Wukari, north eastern Nigeria.

Study design: The studied area is situated in the northwestern part of Wukari Local Government Area of Taraba State, North-East Nigeria. The hydrology of the area provide an atmosphere for the cultivation of crops and fresh water for fishing. The soils and food crops samples were collected in the month of May, 2018.

Methodology: Edible parts of plants such as leaf, stem and seed were collected from Soybeans (*Glycine max*), Guinea corn (*Sorghum bicolor*), Millet (*Penniselum typhoides*), Spinach (*Amaranthus*) and Tomato (*Lycosipinus esculentum*). Soil and plant samples were analysed for trace elements by using Atomic Absorption Spectrophotometer after sample dissolution with a mixture of acids (HNO_3/HCl in a ratio of 1:3 v/v).

Results: The concentrations ($\mu\text{g/g DW}$) of the trace elements in food crops were in the following order: $\text{Se} > \text{Fe} > \text{Mn} > \text{Cr} > \text{Cu} > \text{Pb} > \text{Al} > \text{As}$ while the mean concentration of trace elements in soil are in the order $\text{Mn} > \text{Fe} > \text{Se} > \text{Pb} > \text{Cr} > \text{Cu} > \text{Al} > \text{As}$. The bio-accumulation of trace elements in all food crops were in the range: Se (0.250 – 20.88 $\mu\text{g/g DW}$), Al (0.250 – 0.980 $\mu\text{g/g DW}$), As (0.070 – 0.620 $\mu\text{g/g DW}$) and Pb (0.020 – 0.090 $\mu\text{g/g DW}$).

Conclusion: The Health Risk Index of As, Cr and Fe in spinach and Guinea corn were > 1 . A Significant positive inter element correlation exists between Se and Al thus suggesting similar source of pollutants in either soil or plants. The study revealed that food crops grown on farmlands around mining areas are not safe for consumption.

Key words: Bioaccumulation, concentration, grains, vegetable, soil, trace elements.

1. INTRODUCTION

Environmental pollution has become an issue of great concern due to the great consequences it presents to humans and the entire ecosystem. Trace element pollution has become a serious problem in the vicinity of mining sites [1]. Pollution by trace metals is particularly a serious problem because metals are non-biodegradable and thus tend to persist indefinitely in the environment. Thus, pollution of trace metals is of great concern in the environment and human health. Anthropogenic activities are a major source of heavy metal contamination which includes agricultural crop residue, emission from industries and vehicular emission [2]. Trace metal pollution has become a serious problem in the vicinity of mining sites. Toxic trace metals such as Pb, Cu, Cr, Cd and As in wastewater drained from tailing ponds contaminate

agricultural soils. These metals are deemed to threaten human health and pose a cancer risk to humans [3]. Trace metals can be readily adsorbed by vegetable roots, and can be accumulated in the edible parts of vegetables at high levels, regardless of the metal concentration in the soil [4]. High background of many trace elements in soils has been traced to extremely high concentrations of these elements in the parent materials [5]. The most widely recognized pathway of animals and human exposure to soil contamination is the soil to plant transfer of trace metals. An assessment of the environmental risk due to soil pollution especially heavy metals is of particular importance for agricultural and non-agricultural areas. Because heavy metals, which are potentially harmful to plants, soil microorganisms and human health persist in soils for a very long time. When the heavy metals present in the natural condition they do not act as toxic up to certain extent. When the concentration reaches the maximum level or up to the final permissible level heavy metals will be converted in to toxic in nature and it will lead to the dangerous effects on the surrounding system [6].

The transfer of trace elements from soil to plant is usually considered as an indicator of the plant accumulation behaviour. A number of reports have confirmed the transfer of trace metals from contaminated soil to plants and from plants to livestock [7]. The mobility and phyto availability of metals depend on their chemical nature. Also, some species of plant have the capacity to accumulate high concentrations of certain elements. Other factors that influence uptake of these elements by plants include pH, organic matter, cation exchange capacity [8].

The study focused on investigating the concentrations of trace elements on soil and food crops and compared results with World Health Organisation permissible limits. Hence, determine their bioaccumulation in the food crops to ascertain the levels of soil contamination. The soils and food crops samples were collected on 3rd May, 2018.

2. MATERIALS AND METHODS

2.1 The Study Area: The studied area (Akwana) is situated in the northwestern part of Wukari Local Government Area of Taraba State, North-Eastern Nigeria. It lies between Latitudes 7° 47"N and 7° 52"N and Longitudes 9° 13"E and 9° 17"E. The area is endowed with mineral resources among which are economic deposit and lead/zinc-barytes mineralisation along the Middle Benue Trough. Galena mining is the predominant activities in the area since 2005 to date. The region lies within the Guinea Savannah and the tropical climate (much less rainfall in winter than in summer), rich alluvial soils for the cultivation of most staple foods and cash crops, grazing land for animals and fresh water for fishing. The geology of the entire area reveals few outcrops of gneiss in-land which form a part of the Pan-African basement in the northern parts. The dominant rock types are sedimentary rocks of the Asu River Group formation with a few indications of the Keana formation characterized by coarse-grained sandstone and bands of shale in the eastern area. Further down in the southern and southeastern parts of the area reveals more exposures of gneisses, extensive superficial cover and poor exposures of the carbonate rocks

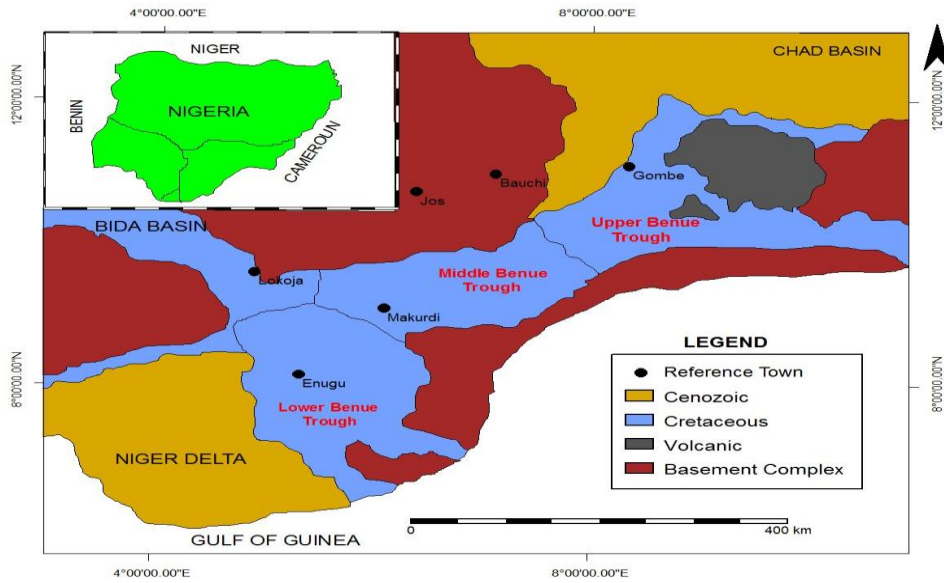


Fig. 1 Map of the Benue Trough of Nigeria.

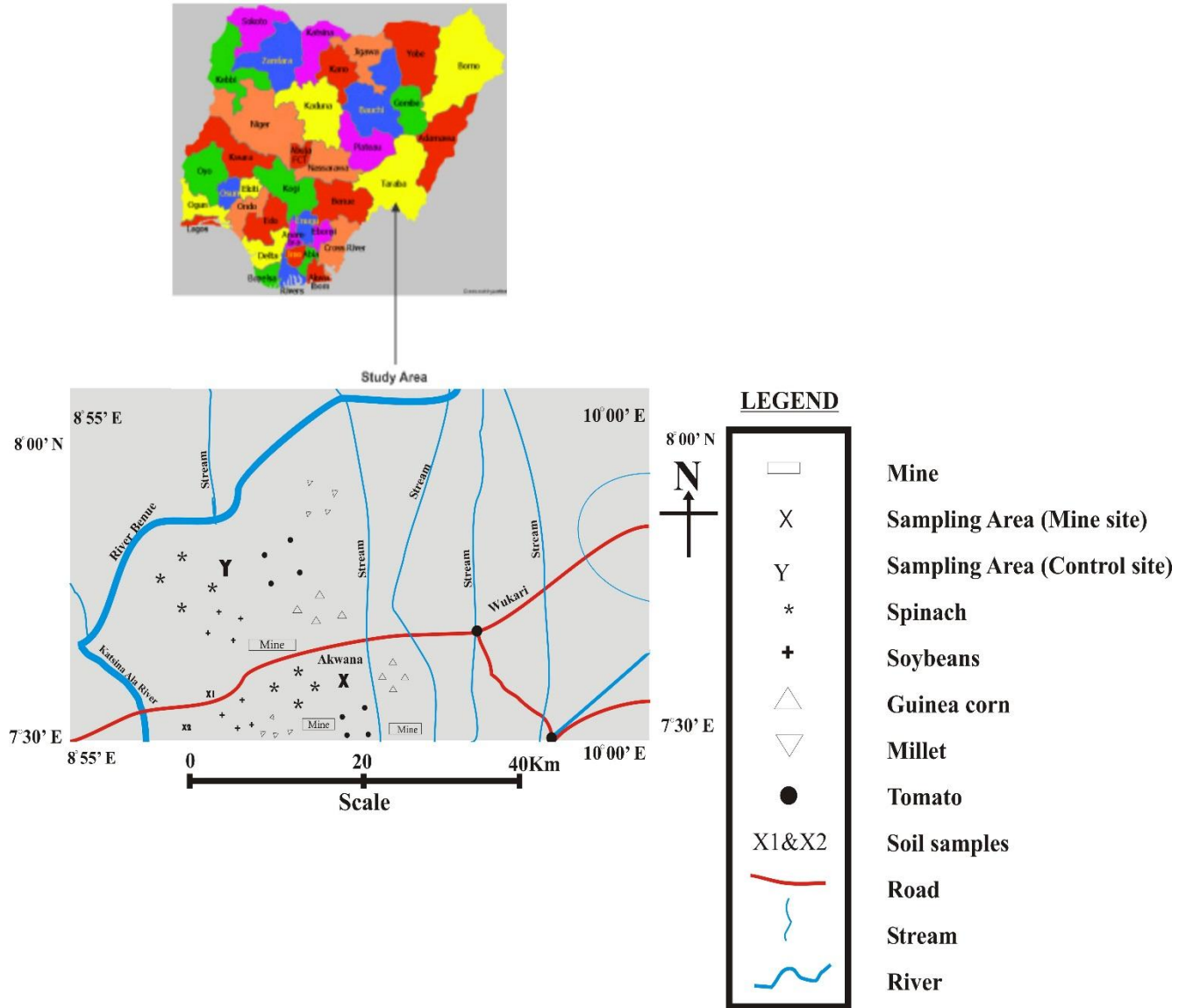


Fig 2: Map of the Study Areas.

2.2 Collection and Treatments of Plant Samples

A 100 g each of twenty (20) food crops samples were collected randomly from the two study areas, X and Y. Where X is farms around the galena mining areas and Y is the adjoining areas of about ten kilometers to the mine as control. The food crops (grains and vegetables) samples from mines areas X, are Spinach (*Amaranthus*) labelled as Spinach X1/X2, Soybeans (*Glycine max*) designated as Soybeans X1/X2, Guinea corn (*Sorghum bicolor*) labelled as Guinea corn X1/X2, Tomato (*Lycopersicon esculentum*) were assigned Tomato X1/X2 and Millet (*Pennisetum typhoides*) are labelled Millet X1/X2 while food crops (grains and vegetables) samples from control areas Y, are Spinach Y1/Y2, Soybeans Y1/Y2, Guinea corn Y1/Y2, Tomato Y1/Y2 and Millet Y1/Y2 respectively. The number 1 and 2 represent sampling points within the mine and control areas.

The raw samples (spinach and tomato) was oven dried at 40 °C for several days and then stored in black polythene bags (about 285 Kg). The dried samples was ground in an impact pulveriser mill to pass through a 300 µm sieve and extruded into polythene bags. This coarse fraction was then further processed in an air jet mill, resulting in a particle size below 50 µm. The samples was then stored in a polythene bag (AQCS, 2000). Equal portions of the grains samples (guinea corn, millet and soybeans) were mixed together to form a representative samples and stored in clean polythene bag. The samples were taken to the laboratory, washed with deionized water to eliminate soils, dust and microbes. The cleaned samples were then dried in an electric oven at 90° for five days. The dried samples were homogenized by grinding in a ceramic coated grinder and sieved with 2mm mesh size. The dried samples were stored in a clean polythene bag prior to digestion [9].

2.2.1 Digestion of Plant Sample

A 1.000 g of the powdered spinach was digested with 10 mL mixture of analytical grade acids HNO₃: HClO₄ in the ratio 5:1. The digestion was performed at a temperature of about 90 °C for 30 minutes in a fume cupboard until clear solutions were obtained. Digested sample was allowed to cooled, filtered into a 100 mL volumetric flask, and made up to the mark with deionized water then taken for AAS analysis. The same procedure was repeated other plant samples [10].

2.3 Collection and Treatments of Soil Samples

A total of 2.000 kg soil samples were collected randomly from two farms around the galena mining areas at a distance of 500 meters apart. The samples were labelled X₁ and X₂ respectively. The alphabet X represents mine area while number 1 and 2 represents sampling points within the area. The samples were collected with the aid of a clean stainless steel shovel from 0-20cm depth and air dried for seven days. The samples were thoroughly mixed in a clean plastic container to produce a homogeneous soil composite and were pulverized with mortar and pestle, sieved at <4 mm [11].

2.3.1 Digestion of soil sample

A 1.000 g of the finely ground soil samples was placed into a kjeldahl flask and 10 mL of aqua regia (a mixture of 1:3 HNO₃/HCl v/v) was added, the mixture was heated at 70 °C on hot plate for 3 hours in a fume hood. The digest was cooled and filtered into a 100 mL volumetric flask, and made up to the mark with deionized water then taken for AAS analysis. This procedure was repeated for all the soil samples [5].

Trace elements concentrations in the digests of soil and food crops samples were determined using Varian AA240 Atomic Absorption Spectrophotometer equipped with Zeeman's background correction (SR-BDG). Triplicate determination were made for all samples.

2.4 Bio-accumulation factor (BAF)

The food chain pathway is recognized as one of the major pathways for human exposure to soil contamination. Bio-accumulation factor is an index of the ability of the vegetable to accumulate a

particular metal with respect to its concentration in the soil substrate [12]. It was calculated using equation 1 below

$$BAF = \frac{C_{Mplant}}{C_{Msoil}} \dots\dots\dots (1)$$

Where, C_{Mplant} represent trace elements concentration in edible part of plant and C_{Msoil} is the concentration of trace elements in the soil.

2.5 Daily intake of metals (DIM)

The daily intake of heavy metal was calculated by using following formula, [13].

$$DIM = \frac{C_{metal} \times D_{food\ intake} \times C_{factor}}{B_{average\ body\ weight}} \dots\dots\dots (2)$$

Where C metal, D food intake, B average weight and C factor represent heavy metal concentration in plant ($\mu\text{g g}^{-1}$), daily intake of vegetable ($\text{gm day}^{-1} \text{ person}^{-1}$), average body weight (kg) and conversion factor (0.085) respectively. The conversion factor was used to convert fresh green vegetables weight to dry weight, as described by [14]. The average body weight was considered to be 60 kg by conducting survey of 105 adult (male and female) people from study areas in each was determined by formal interview conducted with people of study areas during period of sampling. The average daily vegetable (spinach), tomatoes, soybeans, guinea corn and millet in take for adult were considered to be 200, 50, 35, 400 and 350 $\text{gm day}^{-1} \text{ person}^{-1}$ which was determined by formal interview conducted with people of study areas.

2.6 Health Risk Index (HRI)

The value of HRI depends upon the daily intake of metals (DIM) and reference oral dose (Rf_D), which was computed as described by [15]. The HRI less than 1 means exposed population said to be safe [16]. Rf_D value for Al, As, Cr, Cu, Fe, Mn, Pb and Se is 7.0, 0.0003, 0.003, 0.004, 0.007, 0.140, 0.004 and 0.005 $\mu\text{g/g bw /day}$ respectively.

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

2.7 Data Analysis

Data obtained were subjected to statistical tests of significance using the one way analysis of variance (ANOVA) to assess significant variation in the levels of the trace elements. Probability less than 0.05 ($p < 0.05$) was considered statistically significant. Pearson's correlation coefficient analysis was used to determine the association between the trace elements in the samples at $r = 0.01$. All statistical analyses were done by SPSS 17.0 for windows.

3. RESULTS AND DISCUSSION

The mean concentrations of trace elements in soil from points X_1 and X_2 are shown below.

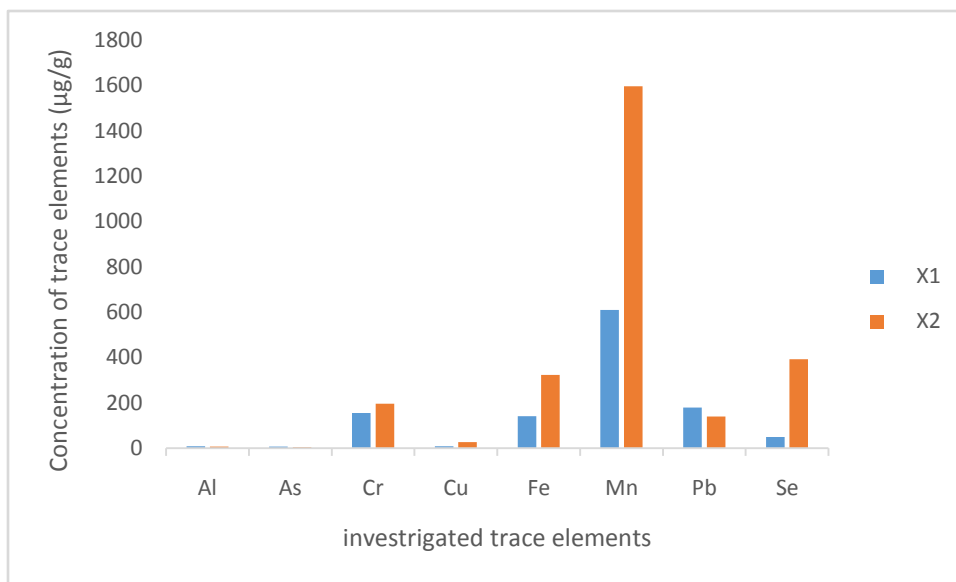


Figure 3: Concentration of trace element in soil from sample X_1 and X_2 .

The two soil samples displayed maximum levels of Mn, Fe, Se, Cr and Pb as showed in figure 1 above. However, Se concentration was higher in point X_1 than X_2 . Al, As and Cu showed low concentrations in both sampling points. The concentration of Mn is within the WHO permissible limits of 2000 $\mu\text{g/g}$ DW in soil. The concentration of Se (50.00 $\mu\text{g/g}$ DW, 392.4 $\mu\text{g/g}$ DW) and Pb (180.1 $\mu\text{g/g}$ DW, 139.3 $\mu\text{g/g}$ DW) determined were above the permissible limit of 10 $\mu\text{g/g}$ DW in soil samples [17]. The concentrations of arsenic (7.38 $\mu\text{g/g}$ DW, 4.76 $\mu\text{g/g}$ DW) in the study areas were below the WHO/FAO permissible limit of 20.00 $\mu\text{g/g}$ DW for agricultural soils. Cr concentrations (155 $\mu\text{g/g}$ DW, 197 $\mu\text{g/g}$ DW) in both sampling point were higher than the WHO/FAO permissible limits (10.00 $\mu\text{g/g}$ DW) in soil and under favorable conditions can be available for plant uptake. The high levels of these element could attributed to the mining activities that are carried in the areas. Similar result was reported by Aremu [18], that the average concentrations of Fe in dump mine soils ranged from 249.7 – 257.63 $\mu\text{g/g}$ DW which are very close to 141.9 – 323.9 $\mu\text{g/g}$ DW recorded in this work. The observed elevated levels of trace elements in the soils are reflected by the high content of Se, Pb, Cr and Fe in most of the food crops. Soil is the prime factor responsible for the trace elements availability to plants. Primarily, the underlying geology determines the content of trace elements in soil through a weathering process over an extended period [4].

To check the reliability of the analytical procedure employed for trace elements determination in food crops, a certified reference material (Cabbage, IAEA 359) of similar composition was analysed in like manner to the samples and replicate analysis of samples together with blank were carried out AQCS, 2000. The measured values and the certified values at 95 confidence interval for six (6) trace elements were presented in table 1. The result showed high value of Mn which is three (3) times the certified value. Cu and Fe has significant values slightly above their corresponding certified values at 95 % confidence

interval. Trace element (Cu and Fe) values extracted from the food crops (vegetables and grains) were more satisfactory than Mn.

Table 1: Analysis of reference material (Cabbage IAEA-359) compared to reference value

Elements ($\mu\text{g/g DW}$)	Se	Cr	As	Mn	Cu	Fe
A. Values	541.1	26.22	1.522	99.91	9.350	167.54
R. Values	-	-	-	31.90	5.670	148.0
95 % CF	-	-	-	31.3 - 32.5	5.49-5.85	114.1-159.9

A Value = Analysed value, R Value = Reference value, CF = Confidence Interval.

The concentration of trace elements in food crops collected from farms in the vicinity of the mine area (X) and control (Y) are presented in Table 2 and 3 respectively. Irrespective of the sampling areas, the results showed that Se, Fe, Mn and Cr with average concentrations of 1043; 998.6, 547.9; 551.2, 353.9; 354.4 $\mu\text{g/g DW}$ in spinach are the most abundant elements assimilated by the food crops while Cu, Al and As showed least levels of assimilation by the various plants as showed in table 2 and 3 respectively.

Generally, the concentration of Mn and Al were higher in spinach, millet and soybeans from sample X than Y as showed in Table 2 and 3. Similar trend was also observed for Se and Pb in spinach. Consequently, the concentration of As, Cr, Se, Cu and Fe in guinea corn, tomato and millet recorded in sample Y were higher than their corresponding sample X.

The concentration of Fe in spinach recorded in this work (542.9 -547.9 $\mu\text{g/g DW}$) is similar to those reported by Ftsum and Abraha [14] which range from 488.0 – 612.0 $\mu\text{g/g DW}$. Zhou et al. [19] investigated trace elements (Fe, Se and Mn) concentrations in 22 vegetable species of six types of vegetables collected from contaminated farmland. It was found that leafy vegetables (spinach) appear to have the highest propensity to trace elements accumulation. Similar observation was made in this study.

Levels of Pb (18.41 $\mu\text{g/g DW}$) in spinach reported by [7] was higher than the 4.230 $\mu\text{g/g}$ in spinach recorded from mine area (X). However, the concentration of Pb in spinach and tomato recorded in this study are higher than those reported by [20] with values 0.028 and 0.091 $\mu\text{g/g DW}$ respectively. The high levels of Se and moderate levels of Pb, Mn and Fe observed in spinach and tomato are supported by [21] that vegetables absorbed or assimilate trace elements than grains. Pb was however not detected in guinea corn, millet and soybeans from both samples.

Table 2: Trace elements Concentrations* ($\mu\text{g/g DW}$) in food crops from mine areas (X)

Samples/Locations	Al	As	Cr	Cu	Fe	Mn	Pb	Se
Spinach X1	5.800	0.200	11.79	13.48	542.9	353.9	4.200	1043
Spinach X2	6.700	2.410	39.00	8.830	547.9	286.7	4.260	957.4
Soybeans X1	4.570	0.600	28.17	14.70	36.34	90.96	BDL	700.6
Soybeans X2	2.560	1.300	34.70	15.59	27.94	70.02	BDL	447.9
Guinea Corn X1	3.130	1.380	34.45	10.20	118.8	47.15	BDL	383.1
Guinea Corn X2	3.090	1.410	16.83	8.720	117.1	29.82	BDL	433.2
Tomato X1	4.340	2.200	29.15	0.590	141.8	35.25	6.560	462.9
Tomato X2	3.200	3.190	29.05	3.950	118.2	23.28	6.080	381.1
Millet X1	4.000	1.210	19.06	8.910	12.71	30.75	BDL	299.3
Millet X2	3.980	1.280	19.98	8.570	13.01	31.22	BDL	301.2

MEAN**	4.140	1.520	26.22	9.350	167.7	99.91	5.280	541.1
STD	1.290	0.870	8.880	4.630	205.0	119.1	1.220	267.5

*values are averages of two replicate (n = 2) for each sample, **values are overall mean of average concentrations of trace elements in all the samples, STD = standard deviation, BDL = Below Detection Limit.

This may be due to the fact that Pb concentration was very high in the residual phase which limits its mobility as reported by [10] who conducted speciation of heavy metals on soil from the study area (Akwana). The concentrations of Pb in spinach obtained from sample X are higher than the 0.300 µg/g DW permissible level while those in sample Y are within the threshold limits. High level of Pb causes disorders in the heart, kidneys, reproductive and nervous system, reduced body immune system, memory deterioration and death [22; 23].

Table 3: Trace elements Concentrations* (µg/g DW) in food crops from control areas (Y).

Samples/Locations	Al	As	Cr	Cu	Fe	Mn	Pb	Se
Spinach Y1	0.100	4.800	12.70	14.61	543.9	354.4	0.002	998.6
Spinach Y2	6.800	0.300	40.50	9.800	551.2	276.7	0.004	879.7
Soybeans Y1	5.3000	2.600	31.80	15.11	387.6	89.50	BDL	702.4
Soybeans Y2	2.700	0.800	37.60	11.76	124.9	69.70	BDL	450.8
Guinea Corn Y1	3.300	1.400	35.70	17.18	118.7	48.30	BDL	389.2
Guinea Corn Y2	3.500	2.000	17.60	11.07	128.8	30.60	BDL	427.7
Tomato Y1	4.700	3.200	30.30	8.850	152.1	35.40	0.004	478.5
Tomato Y2	3.4000	2.500	30.80	1.620	18.2	24.80	0.001	387.9
Millet Y1	3.700	3.900	29.70	16.35	109.4	45.20	BDL	411.6
Millet Y2	3.100	2.200	18.50	12.02	112.5	31.50	BDL	391.1
MEAN**	3.660	2.370	28.52	11.84	224.7	100.6	0.003	551.8
STD	1.760	1.370	9.240	4.540	194.1	116.4	0.002	225.9

*values are averages of two replicate (n = 2), **values are overall mean average concentrations of trace elements in samples, STD = standard deviation, RANGE = minimum to maximum average value, BDL = Below Detection Limit.

This study revealed high concentration of Cr (11.75 – 40.50 µg/g DW) in spinach than other food crops (table 2 and 3). However, results reported by [24] showed that, the average level of Cr in spinach and tomato (2.300; 1.500 µg/g DW) were less than (26.80; 29.20 µg/g DW) those recorded in this research.

From the Levene's test for equality of variances (Table 4), with the exception of Pb ($p = 0.000$), other elements such as Se ($p = 0.600$), Al ($p = 0.674$), As ($p = 0.242$) have p – value greater than 0.05 level of significance. This means that the variances are equal and there is no significance difference ($p > 0.05$) in the variances of areas adjoining the mine used as control (Y) compared to the mine area (X).

Table 4: Test for equality of variances and means of trace elements in plants

	Al	As	Cr	Cu	Fe	Mn	Pb	Se
F	0.182	1.466	0.002	0.005	0.044	0.004	80.541	0.284
Sig.1tailed*	0.674	0.242	0.966	0.946	0.836	0.948	0.000	0.600
Sig.2tailed**	0.498	0.114	0.577	0.241	0.531	0.989	0.029	0.925
Df	18.00	18.00	18.00	18.00	18.00	18.00	18.00	18.00

*test for equality of variances, **test for equality of means

The T- test for equality of means (Table 4) revealed significant difference ($p < 0.05$) in the mean level of Pb in the mine area compared to the mean level of Pb in area adjoining the mine used as control. Se ($p = 0.925$), Aluminium ($p = 0.498$), As ($p = 0.114$) have p – value greater than 0.05 level of significance, meaning that there is no significant difference ($p > 0.05$) between the mean levels of these elements in food crops from areas adjoining the mine used as control and the mine area.

Table 5: Inter-element Pearson's correlation for food crops from the study area.

	Cu	Fe	Cr	Se	Al	As	Mn	Pb
Cu	1							
Fe	0.095	1						
Cr	0.071	-0.304	1					
Se	0.406*	0.658**	-0.106	1				
Al	0.026	0.665**	-0.067	0.789**	1			
As	-0.735**	0.024	0.032	-0.482*	-0.037	1		
Mn	0.334	0.303	0.149	0.712	0.753*	-0.273	1	
Pb	0.051	-0.122	0.059	0.136	0.257	0.014	0.462*	1

*Pearson's correlation significant at $p < 0.05$, **Pearson's correlation significant at $p < 0.01$

The correlation investigation is a bivariate process which is useful to define the relation among two dissimilar elements. The great correlation coefficient ($r =$ higher than 0.700) demonstrate strong correlation among two element [25]. Person Correlation coefficient data for trace elements in soils are depicted in Table 5 above. From Coefficients of Pearson Correlation (r) data reveal that a strong positive correlation (p , 0.010) was observed between Se & Al ($r = 0.789$) as well as between Mn & Al ($r = 0.753$). The observed relationship between these elements may signify similar source of these elements in food crops (plants). The observation may be attributed to the geology of the area considering the high mean levels of these elements in soils where the samples were collected.

Table 6: Pearson's correlation study of metals in plant, soil samples

	Al	As	Cr	Cu	Fe	Mn	Pb	Se
soil/plant	-0.007	-0.437	-0.381	-0.519*	0.437	-0.022	-0.237	0.096

*correlation significant (2 tailed) at $p = 0.05$, **correlation significant (2 tailed) at $p = 0.01$

Generally, there is no strong correlation between elements abundant in the soil and elements abundance in plants. However, significant negative correlation was observed for Cu in plant and soil at $p = 0.05$ (Table 6).

Table 7: Comparison of measured values ($\mu\text{g/g DW}$) and FAO/WHO guidelines on food crops

Samples	Al	As	Cr	Cu	Fe	Mn	Pb	Se
Spinach	6.250	1.31	25.40	11.15	545.5	320.3	4.230	1000
Tomato	3.770	2.70	29.10	2.270	129.3	29.27	6.320	420.0
Soybeans	3.570	0.95	31.44	15.15	32.14	80.49	<0.0001	574.3
G/corn	3.110	1.40	25.64	9.460	117.9	38.49	<0.0001	408.5
Millet	3.990	1.25	19.52	8.740	12.86	30.99	<0.0001	300.2
FAO/WHO 2001	NA	NA	2.300	40.00	425.0	500.0	0.300	NA

NA = Not Available

From Table 7 above, the result revealed high concentration of Se, Cr, Fe and Pb in most of the food crops while Cu, Al and Mn concentration were low.

The concentration of Fe determined in spinach were above the WHO/FAO threshold limit of 425 µg/g. According to [26] the ratio of Fe/Mn in vegetal tissue should be between 1.5 and 2.5 since both elements are involved in metabolic processes hence, they must be present in suitable proportions for adequate plant growth. In the present study the ratio of Fe/Mn were 1.703 in spinach and 2.417 in tomato.

Spinach concentrations were very high compared to grains (guinea corn, soybeans and millet) grown in the study areas. This result is supported by Fan [27] that trace element concentrations in non-leafy vegetables were less than that in leafy vegetables and previous studies have shown that the transfer ability of trace elements from soils to vegetables was stronger in leafy vegetables compared with non-leafy vegetables. The concentration of Se in spinach was higher than other food crops and Selenium is an important nutrient for humans and animals, but can be harmful when taken in too much quantity. In animals, Se acts as an antioxidant and supports in reproduction, immune responses, thyroid hormone metabolism [20].

The concentration of Cr in all the food crops was above the WHO/FAO permissible levels of 2.300 µg/g. The concentrations of Cr in spinach observed in this work are high compared to 3.620 - 14.58 µg/g DW reported by [28] in their research. The concentrations of Pb in spinach are above the WHO/FAO permissible limit of 0.300 µg/g (WHO/FAO, 2001). High levels of Pb in vegetables was also reported by Sotiris et al. [29] in their work with concentration ranges from 0.490 to 1.370 µg/g DW. [30], also reported high concentration of Pb (10.5 µg/g DW) in spinach than the result obtained in this work. Therefore, spinach should not be encouraged to grow in soils which are contaminated with Pb.

Soybeans accumulated highest amount of Cu compared to other trace elements while tomato has the least. The concentration of Cu in this study is within the WHO/FAO permissible limits (table 7). The least levels (0.950 µg/g DW) of As were detected in soybeans followed by millet 1.250 µg/g DW, spinach 1.310 µg/g DW, guinea corn 1.400 µg/g DW and the highest levels was obtained in tomato 2.700 µg/g DW. Arsenic was detected in all the samples analysed but at low levels compared with WHO/FAO permissible limits.

[4] reported in his work that, leafy vegetables grown on contaminated soils accumulate high concentrations of trace elements in their edible parts. Guinea corn and millet are among the important, predominant staple food crops in Wukari Local Government Area of Taraba State, Nigeria. They are usually cultivated in large quantity as they find large application in production of local beers called burukutu or Achen and pito in Jukun language. The level of Se determined was found to be highest in guinea corn, followed by Al and As. Excessive mining activities contribute greatly to the level of trace element in the study areas.

3.1 Bioaccumulation Factor

The bio-accumulation factors showed the extent of trace elements accumulation in food crops which were in the following range: Se (0.250 – 20.88 µg/g DW), Al (0.250 – 0.980 µg/g DW), As (0.070 – 0.620 µg/g DW) and Pb (0.020 – 0.090 µg/g DW).

Table 8: Bioaccumulation Factor (BAF) of trace elements in food crops from mine area (X)

Samples	Al	As	Cr	Cu	Fe	Mn	Pb	Se
Spinach X1	0.760	0.620	0.080	1.620	3.830	0.570	0.020	20.88
Spinach X2	0.980	0.500	0.200	0.330	1.690	0.170	0.030	2.440
Soybeans X1	0.590	0.070	0.150	0.490	0.640	0.070	ND	0.850
Soybeans X2	0.250	0.160	0.220	0.5900	0.040	0.160	ND	0.690
Guinea Corn X1	0.280	0.250	0.210	0.210	0.340	0.250	ND	0.700
Guinea Corn X2	0.420	0.420	0.1100	0.210	0.240	0.420	ND	0.850
Tomato X1	0.360	0.360	0.290	0.010	0.220	0.360	0.090	0.340
Tomato X2	0.520	0.520	0.250	0.080	0.040	0.520	0.080	0.250
Millet X1	0.230	0.230	0.120	0.180	0.040	0.230	ND	0.530
Millet X2	0.380	0.380	0.010	0.120	0.030	0.380	ND	0.570
MEAN**	0.480	0.350	0.160	0.380	0.710	0.310	0.060	2.810
STD	0.240	0.170	0.090	0.470	1.210	0.160	0.040	6.380

ND = Not Determined, *values are mean BAF of metals in samples, STD = standard deviation.

The study showed high bioaccumulation of Se and Al in Soybeans, Guinea corn and Millet. The bioaccumulation of Se is very low tomato while Al has high bioaccumulation value of 0.360 and 0.520 in tomato. Bioaccumulation factor (BAF) for most elements showed a relatively low values (< 1) except in spinach (leafy vegetable) where Bioaccumulation factor value > 1 was recorded for Se, Fe and Cu. This indicates minimal accumulation of trace elements on the plants tissues. From the study, bioaccumulation factor decreases from Se through Fe, Cu Al, As to Pb. This shows that Pb may be less available for plant uptake despite its high concentrations in the analysed soil. The availability of these elements depends on their solubility, mobility and to some extent on type of plant and mechanism for uptake. [20] in their work reported moderate bioaccumulation of Cu and Fe with Bioaccumulation factor value > 1 in selected vegetable crops.

3.2 Daily Intake of Metals (DIM)

The DIM values in µg day⁻¹ through consumption of investigated food crops are given in Table 9 below. The results revealed the sum of daily intakes of Al, As, Cr, Cu, Fe, Mn, Pb and Se by adults in food crops collected from farmlands around the mining areas was found to be 5.955, 2.021, 35.03, 13.77, 238.5, 133.9, 1.647 and 519.9 µg day⁻¹ respectively. The DIM of Se (28.48 - 283.0 µg day⁻¹), Pb (0.448 – 1.199 µg day⁻¹), Cr (1.559 - 14.53 µg day⁻¹), As (0.047 - 0.793 µg day⁻¹), Fe (1.593 - 154.6 µg day⁻¹) and Mn (2.073 - 90.75 µg day⁻¹). However, DIM of Se, Fe, Pb and Mn in spinach were high compared to other food crops. The DIM of As, Cr and Cu were also very high in guinea corn and millet. The DIM of Cr (1.559 - 14.53 µg day⁻¹) in all the food crops is higher than the recommended oral reference dose (RfD) of 1.5 µg day⁻¹ [31]. The values of daily intake of Cr (2.061 - 7.197 µg day⁻¹) in vegetables is higher than those

reported by [32] in their findings which ranged from 0.048 - 0.082 $\mu\text{g day}^{-1}$. The results of this findings for metals consumption irrespective of food crops showed low intake of Cu (13.77 $\mu\text{g day}^{-1}$) and Pb (1.647 $\mu\text{g day}^{-1}$) compared to 38.19 and 2.563 $\mu\text{g day}^{-1}$ reported by [33]. The daily intake of metals through consumption of guinea corn was found to be higher compared to millet and soybeans. Hence, soybeans contained the least values of daily intake of metals.

Table 9: Daily Intake of Metals ($\mu\text{g day}^{-1}$) in food crops.

Samples	Al	As	Cr	Cu	Fe	Mn	Pb	Se
Spinach	1.771	0.371	7.197	3.159	154.6	90.75	1.199	283.0
Tomato	0.267	0.191	2.061	0.161	9.159	2.073	0.448	29.75
Soybeans	0.177	0.047	1.559	0.751	1.593	3.991	-	28.48
G/corn	1.762	0.793	14.53	5.361	66.81	21.81	-	229.8
Millet	1.978	0.619	9.679	4.333	6.376	15.36	-	148.9
Σ DIM	5.955	2.021	35.03	13.77	238.5	133.9	1.647	519.9
% of PDTI	1.985	2.887	77.84	0.459	95.35	0.669	0.769	90.45

PTDI Al = 0.3 $\mu\text{g day}^{-1}$, As = 0.07 $\mu\text{g day}^{-1}$, Cr = 45 $\mu\text{g day}^{-1}$, Cu = 0.003 $\mu\text{g day}^{-1}$, Fe = 48 $\mu\text{g day}^{-1}$, Mn = 0.02 $\mu\text{g day}^{-1}$, Pb = 214 $\mu\text{g day}^{-1}$ and Se = 55 $\mu\text{g day}^{-1}$.

The daily intake of heavy metals (DIM) depend on the concentration of heavy metals in food crops samples. The DIM values reported in this research as showed in table 9 above are very high compared to the findings of [14] with values 0.083, 0.002, 0.028 and 0.0005 $\mu\text{g day}^{-1}$ for Fe, Cr, Cu and Pb. The higher DIM values of Fe and Se than the remaining metals might be due to highest values of concentration of the two metals in the spinach leafy vegetable. Similar results were also observed in [34]. The data obtained for percentage of provisional tolerable daily intake (PTDI) of metals revealed that, consumption of food crops cultivated on farmlands around the mining area has 95.35, 90.45 and 77.84 % of Fe, Se and Cr respectively. Therefore, the daily consumption of average quantity of some of these food crops may pose health risk for consumers. The PTDI recorded for Pb 0.769 % is less than the 8% reported by [35] in his findings. This percentage would not cause any adverse health concerns to consumers.

3.3 Health Risk Index (HRI).

The HRI values for consumption of test food crops collected from the study area are showed in table 10 below. The results revealed that HRI value for Al, Cu, Mn and Pb in all food crops were found to be less than 1.0. The HRI results of As, Cr, Fe and Se in this study were 6.740, 11.67, 34.08 and 24.88. The population is therefore at greater risk of As, Cr, Fe and Se as also reported by [36]. However, [14] very low values of HRI for Fe, Cr, Cu and Pb in spinach (0.119, 0.0002, 0.067 and 0.133) compared those reported in this work (table 10). [33] also reported low value ($\Sigma = 1.515$) of HRI for trace elements in spinach compared to those obtained in in this work.

Table 10: HRI for heavy metals in food crops.

Samples	Al	As	Cr	Cu	Fe	Mn	Pb	Se
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Spinach	0.0003	1.237	2.399	0.079	22.09	0.648	0.299	5.660
Tomato	0.0004	0.637	0.687	0.004	1.308	0.015	0.112	5.950
Soybeans	0.0003	0.157	0.519	0.019	0.228	0.029	-	5.695
G/corn	0.003	2.643	4.843	0.134	9.544	0.156	-	4.596
Millet	0.283	2.066	3.226	0.108	0.911	0.109	-	2.977
ΣHRI	0.287	6.740	11.67	0.344	34.08	0.961	0.411	24.88

The HRI values of As, Cr and Fe in spinach and Guinea corn were greater 1. However, Se has values greater than in all studied food crops. The exceeded values of these metals suggest that food crops grown in the studied areas are not safe for consumption.

4. CONCLUSION.

The concentration of Cr in all food crops was above the FAO/WHO permissible limits, Cu and Mn concentrations were within the threshold limits in all the food crops examined. The high level of Cr and Se is evident in DIM and HRI values calculated. However, the concentration of Pb and Fe in spinach and tomato also outweigh the FAO/WHO permissible limits. The evaluated elements especially Cr and Pb are considered as potentially highly toxic to biological systems and therefore they are of great environmental concern. Significant positive inter element correlation exists between Se and Al thus suggesting similar source of pollutants in either soil or plants. The study revealed that food crops grown on farmlands around mining areas are not safe for consumption.

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