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Ecological Risk of Artisanal Mining on Heavy Metals and Radionuclide Levels of Food Crops and Fruits from a Gold Mining Area in Osun State, Southwest Nigeria.

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Abstract

Concentrations of nine heavy metals and radionuclide in food crops, vegetables and fruits harvested from a mining location were determined and compared with safe limits set by World Health Organization (WHO), Food and Agricultural Organisation (FAO) as well as the United Nations Scientific Committee on the Effects of Atomic Radiation (UNSCEAR). Samples, consisting food crops, vegetables, leaf and fruit were collected randomly at harvesting points from Itagunmodi, a mining village in Atakumosa west local Government, Osun State, Nigeria and compared with similar samples collected from a control site. Heavy metal concentrations in the samples were determined by Atomic Absorption Spectrophotometer (AAS) while the radionuclide concentrations were analyzed by gamma spectrometer. The results of heavy metal analysis of samples were found to exceed the World Health Organization (WHO) permissible limits for food crops and vegetables. The estimated daily intake of these food crops, vegetables and fruit showed that the intake of the toxic metals Pb, Cd, Ni and As in the studied samples were above provisional tolerable daily intake limits. The results obtained from the Gamma analysis showed the highest concentration of ^{40}K, ^{238}U, ^{232}Th occurring naturally in *manihot esculenta*. Annual gonnadial dose equivalent (AGDE). Excess lifetime cancer risk (ELCR) and other hazard indices showed a high probability of specific health issues occurring during a specific lifetime as a result of the effect of gamma radiation on the food samples for both adults and children calling for an urgent need for strict regulations against illegal mining.

Key words: heavy metal, radiations, mining, toxic, regulations, food crops

INTRODUCTION

In recent times, the percentage of gold mineral mined daily in Gold-rich regions of the country has been on the increase. A large percentage of these mining operations have been through small scale and by artisans who has dominated the scene in most part of the country and specifically in the south west part of the country. These artisanal miners are usually in the services of mining companies and do their task independently using their own techniques with the sole aim of reducing the cost of mining while aiming for higher profits. They do not sell their products through traders but operates on the basis of a contract system with companies, which guarantees the purchase of all their productions. In essence, artisanal miners make use of use mostly local or primitive technologies (Figure 1) which gives little or no consideration for environmental safety and management in addition to being time and energy consuming.

The detrimental effects of Gold mining on soil, water, plants in mining environments in Nigeria and the world all over has been tremendous [Alloway and Ayres, 1993] and has always being a major subject of concern. Ranging from the degradation and devaluation of land mass, whose reclamation has always been a major problem thereby leading to loss of land value, to the high-level contribution of contaminating and harmful materials to the environment above desirable levels [Fatoki *et al*, 2002]. In the large-scale environmental degradation caused generally by mining of minerals, especially, Gold, those carried out by artisanal and small scale miners contributes the highest with their crude technologies and practices which results into large scale destruction of soil, vegetation, water and even air.

Another negative effect of gold mining on the environment is its pollution with heavy metals [Makinde *et al*, 2018] as well as increasing the radionuclide concentrations of soil, water and vegetation of the mining environments [Makinde *et al*, 2020]. These naturally occurring elements are known to be toxic at low concentrations and as such detrimental to safety existence of plant, animals and aquatic organisms and man, through ingestion, for survival. Mining of Gold mineral is known to be associated with certain heavy metals such as Pb, Cd, As, Hg, Cr e.t.c, whose concentration is brought to an unsafe level for living organisms through mining, especially, by artisans. High levels of these toxic metals have been reported in vegetations [Ikpi *et al*., 2021], water [Phillip and Bernard, 2020; Aremu *et al*., 2002; Chukwudi *et al*., 2002] and soils [Fagbenro *et al*., 2021; Mbet *et al*., 2020] around mining environments. Similarly, different levels of hazards have been assessed in soils, water, sediments and vegetations by determining the activity concentrations of radionuclides in the different environmental facets of mining environments.

The safety or otherwise of mine tailings as well as soils from mining areas have been reported and interpreted to quantify their lifetime cancer risks, external and internal hazard indices and gamma doses and other radiation hazards associated [Muhammad *et al*, 2020; Kolo *et al*, 2017]. Essentially, transfer of nutrients from soil to plant, is a major way through which heavy metals and ionizing radiations gets to man through the food chain or water consumption, either directly or via irrigation [Muyiwa *et al*., 2022] to particularly demonstrate the risks involved in high concentrations of heavy metals and other contaminants around mining environments. The present study reports such risk level associated with mining of the precious metal in the environment. The mining village is known to be rich in cultivation of agricultural products like cocoa, cassava, yam, plantain, vegetables and fruits which has recently become secondary as a result of high-level artisanal mining by a large percentage of youths in the area.

Figure i: Pollution of Stream water and sediment by washing of dug 'Gold' Debris

MATERIALS AND METHODS

The study area is Itagunmodi, a farming and mining village, located in Atakumosa West Local Government Area (longitude 4° 40' - 4° 60' E and latitude 7° 15' - 7° 25'N) and covers an area of 577km^2 with a population of 68, 643 (2006 census). The site selected for collection of the control samples for this study is Tonkere, a village in Ife Central Local Government Area of Osun state, where there is no physical evidence of gold mining or any other metal. Samples were collected randomly from the study area and the control site. Nine samples, consisting of Food crops, Fruits and Vegetable, were collected at random at selling points in the study area. Each sample was packed separately in labeled polythene bags from where they were transported to the laboratory for further treatment. In the laboratory, the samples were washed clean of soils, edible parts of the samples were collected and dried appropriately, first in the air and later oven dried at 45^{0}C. Determination of heavy metals in collected food crops, fruits and vegetables from the study sites and control was done using the PG 990 Atomic Absorption Spectrophotometer (AAS) available at Centre for Energy Research and Development (CERD), Obafemi Awolowo University, Ile-Ife for the determination of nine (9) heavy metals viz: Pb, Cd, Zn, Cr, Mn, Fe, Cu, Ni and As by flame atomization, using air-acetylene flame and single element hollow cathode lamp after samples digestion using aqua-regia acid mixture.

Metal Recovery Experiment

The quality of the heavy metal determination by Atomic Absorption Spectrophotometric (AAS) analysis procedure described above was assured by carrying out a metal recovery experiment. This was achieved by spiking a known amount of each sample with known concentration of the metals from stock solutions and recovering the metals using the same analytical technique **(**Asare *et al*, 2019). The percentage recovery was calculated as

$$\% \text{ Recovery} = (A\text{-}B)/C \times 100 \quad (1)$$

(Where A = Concentration of the spiked sample, B = Concentration of the un-spiked sample and C = Concentration of the metal ion added)

Determination of Radionuclide Concentration

Gamma ray spectrometry was used to determine the concentration of radionuclide in the samples. The activities of various radionuclides were determined in Bq kg^{-1} from the count spectra obtained from each of the samples using the gamma ray photo peaks corresponding to energy of 1120.3 keV (214Bi), 911.21 keV (228Ac) and 1460.82 keV (40K) for 238U, 232Th and 40K, respectively. The risk associated with the health of miners and people in the area were estimated using the estimated daily intake of metals (EDI and target hazard quotient (THQ) for non-carcinogenic risk. The risks were calculated for adults (18-60yrs) with an average body weight of 55.9Kg and children (4-16yrs) with an average age of 35Kg [Aremu *et al*, 2002; Chukwudi *et al*, 2002]. Using 0.345Kg/person/day as daily intake of food crops and fruits for adults and 0.118Kg/person/day for children, the EDI was estimated as:

$$EDI = C_{metal} \times D_{food\ intake} / B_{average\ weight} \quad (2)$$

while the THQ was estimated as:

$$THQ = EDI/RFD \quad (3)$$

Where EDI is the estimated daily intake (µg/kg bw/day), C_{metal} is the heavy metal concentration in plants (ppm), $D_{food\ intake}$ is daily intake of food crops and vegetables (kg/person/day), $B_{average\ weight}$ is average body weight (kg/person) and THQ is the target hazard quotient, , RFD is the oral reference dose for metals under study: Cd (0.001), Pb (0.0035), Cu (0.04), Zn (0.03), Cr (0.003), Mn (0.14), Fe (0.7), Ni (0.02), As (0.0003) (mg/kg/day) [Fagbenro et al, 2021].

Estimation of the radiological hazard risks was done by calculating the Absorbed Gamma Dose Rate,

$$D\ (nGy/h) = 0.462A_U + 0.604A_{Th} + 0.041A_K \quad (4)$$

Where A_K, A_{Th}, A_U are the activity concentration of ^{40}K, ^{232}Th and ^{238}U in Bq/kg respectively.

Annual Effective Dose Equivalent (AEDE) in mSv/y resulting from the absorbed dose values (ADR) was calculated using the following formula (UNSCEAR, 2000)

$$AEDE\ (mSv/y) = ADR\ (nGy/h) \times 8760h \times 0.7Sv/Gy \times 0.2 \quad (5)$$

$$AEDE\ (mSv/y) = ADR\ (nGy/h) \times 0.00123 \quad (6)$$

The annual gonnadial dose equivalent (AGDE) was determined by the following equation

$$AGDE\ (uSv/y) = 3.09\ (U) + 4.18\ (Th) + 0.314\ (K) \quad (7)$$

(Where (U), (Th) AND (K) are the radioactivity concentration of 238U, 232Th, 40K in the samples)

While the excess lifetime cancer risk (ELCR) was calculated as:

$$ELCR = AEDE \times DL \times RF \quad (8)$$

(Where AEDE, DL and RF are annual effective dose equivalent, duration of life (54.5 yrs) and risk factor (0.05S/v) i.e. fatal csancer risk per Sievert).

RESULTS AND DISCUSSION

Table 1: % Recovery of Metals from Spiking Experiment

	Metals	Av. % Recovery
1	Zn	90.11
2	Cd	73.72
3	Pb	69.09
4	Cu	91.26
5	Mn	88.14
6	Cr	90.61
7	Ni	90.18
8	As	74.94
9	Fe	89.16

The result obtained from the recovery experiment of each of the nine metals of the spiked plant sample to determine the quality of the analytical procedure is shown in Table 1. The mean percentage recoveries ranged from 69.09% in Pb to 91.26 % in Cu metal. These recoveries are reasonable and showed the quality of the Atomic Absorption Spectrophotometer (AAS) procedure used for the heavy metal analysis (Asare *et al*, 2019; Harvey, 2000; Machado and Griffith, 2005). The concentration of heavy metals recorded in all the commonly consumed food samples collected from the mining area and the control site are as shown in Table 2 (food crops and fruits) and Table 3 (leaves and vegetables).

The Table also includes safe/permissible limits set by the World Health Organisation (WHO, 1996) as well as the Food and Agricultural Organization (FAO, 2006) for heavy metals in food samples. In all, concentrations of As, Cd, Cr, Cu and Mn were above safe limits in the studied food crops and fruits (Table 2) while Cd, Cr, Pb, Mn, Ni and As recorded higher concentrations than the recommended safe limits by the WHO/FAO in the vegetables Table 3. While high values of heavy metals recorded in control samples might be attributed to the use of farm chemicals as the site is also an agricultural area with similar food crops being planted, the high values however recorded in the study samples can be linked to the effects of mining operations in addition to the use of farm chemicals as these metals are daily turned out from the digging of soil for gold metal and are washed into streams where they are taken up by vegetables and other plants. Similar study carried out by Makinde *et al*., 2018 in the study area also reported pollution with these heavy metals. Results obtained for all the heavy metals considered showed samples from the study site to be higher in concentrations of toxic metals when compared with results from control samples. Cd, Cr, Cu and As were found to exceed the permissible limit both in the samples obtained from mining site and samples obtained from control site. However, Fe, Zn, Mn, Ni were lower than the maximum allowable limit. The estimated daily intake of selected metals from the consumption of the samples per day for adults and children is presented in Table 4. A tolerable daily intake limits for Mn as endorsed by the National Research Council of Canada (NRC) ranges from 2-5mg/day for children above 10years of age and up to 11mg/day for adults up to 70years of age [Muhammad *et al*, 2020; Kolo *et al*, 2017]. In the study, results showed the estimated daily intakes of manganese for adults and children to be 0.012-0.023 mg/kg/day, 0.007-0.013 mg/kg/day respectively. These values are much lower than the daily requirement. A little Mn Daily intake is required for proper development and

Table 2: Heavy Metal Concentration (in mg/kg) of Food Crops and Fruit from Mining and control Site

		Cd	Cr	Fe	Zn	Pb	Cu	Mn	Ni	As
Dioscorea alata (Water yam)	MS	2.9±0.0003	4.3±0.0007	40±0.0016	33±0.0010	1.0±0.0003	55±0.0016	2.1±0.0003	2.1±0.0003	1.0±0.0004
	CS	1.8±0.0001	2.5±0.0002	26±0.0003	18±0.0006	0.5±0.0001	30±0.0002	2.0±0.0007	1.8±0.0002	0.2±0.0001
Colocasia esculenta (Cocoyam)	MS	3.3±0.0005	4.0±0.0008	39.5±0.0011	30±0.0011	0.8±0.0002	69±0.0019	3.0±0.0005	2.7±0.0003	0.9±0.0004
	CS	1.7±0.0005	3.0±0.0008	28±0.0007	19±0.0002	0.8±0.0002	28.5±0.0007	2.2±0.0007	1.6±0.0008	0.8±0.0003
Manihot esculenta (Cassava)	MS	3.7±0.0006	4.4±0.0007	41.5±0.0014	31±0.0009	1.0±0.0004	63±0.0012	2.6±0.0005	2.5±0.0004	1.7±0.0005
	CS	2.0±0.0002	2.7±0.0002	27±0.0002	21±0.0005	0.5±0.0002	25.5±0.0003	1.8±0.0005	1.5±0.0003	0.5±0.0001
Musa paradisiaca (Plantain)	MS	3.5±0.0008	4.8±0.0007	42.5±0.0017	35±0.0010	1.6±0.0006	66.5±0.0016	3.4±0.0006	3.0±0.0005	1.4±0.0004
	CS	1.6±0.0002	2.9±0.0004	30±0.0004	25±0.0010	0.7±0.0002	32±0.0005	1.9±0.0006	1.8±0.0008	0.7±0.0003
Ananas comosus (pineapple)	MS	1.8±0.0003	3.3±0.0004	46.5±0.0020	23±0.0004	0.7±0.0002	56±0.0012	2.7±0.0005	2.5±0.0004	0.7±0.0003
	CS	1.1±0.0005	1.5±0.0005	23±0.0011	20±0.0002	0.4±0.0003	11.5±0.0007	1.4±0.0005	1.1±0.0008	0.3±0.0004
Permissible limit		0.2	0.2	425.5	60.0	5.0	40.0	2.0	3.84	0.15

(MS: mining samples, CS: control samples)

Table 3: Heavy metal concentration *(mg/kg)* in Vegetables and Leaf Grown around the Mining Area and controls

		Cd	Cr	Fe	Zn	Pb	Cu	Mn	Ni	As
Senecio biafrae (woorowo)	MS	1.9±0.0004	5.2±0.0010	36±0.0010	12.5±0.001	0.8±0.0004	48.0±0.0010	1.9±0.0002	1.8±0.0002	0.7±0.0003
	CS	0.8±0.0002	1.6±0.0003	18±0.0003	10±0.0001	0.2±0.0001	9.5±0.0002	1.2±0.0005	1.1±0.0002	0.2±0.0001
Corchorus olitorius (ewedu)	MS	2.0±0.0005	3.0±0.0008	25±0.0008	10±0.0004	1.1±0.0005	46.0±0.0007	2.5±0.0004	1.8±0.0003	0.3±0.0001
	CS	1.0±0.0002	1.7±0.0002	19±0.00004	12±0.002	0.2±0.0002	8.0±0.0003	1.7±0.0004	1.2±0.0003	0.2±0.00001
Amaranthus hybridus (tete)	MS	2.6±0.0004	3.1±0.0006	30±0.0006	17±0.0006	0.7±0.0002	58.0±0.0010	3.8±0.0004	2.2±0.003	0.7±0.003
	CS	0.7±0.0001	1.5±0.0002	21±0.0003	12±0.0010	0.2±0.0001	5.0±0.0002	1.0±0.0003	1.0±0.0003	0.2±0.0002
Thaumatococcus daniellii (ewe eran)	MS	1.8±0.0003	3.3±0.0006	33.5±0.0010	15.5±0.0004	1.5±0.0005	59.5±0.0012	2.4±0.0004	2.0±0.0003	1.1±0.0003
	CS	0.8±0.0003	2.0±0.0002	15±0.0005	10±0.0003	0.3±0.0002	10.0±0.0005	1.2±0.0004	1.0±0.0002	0.3±0.0002
Permissible limits		0.2	0.2	150	5-99.4	0.3	73.3	2.0	1.5	0.15

Results was expressed as actual concentration ± SD (MS represent metal concentration in mining samples while CS represent metal concentration in control samples good health in humans while a deficient in Mn could cause poor growth, impaired reproduction and serious nervous system problems [Muyiwa *et al* 2022]. A daily intake of zinc is vital to keep a stable condition since the body has no particular Zn accumulation system. Zn also reduces the toxicity of cadmium and copper, but its deficiency or extremely high levels may develop vulnerability to carcinogenesis [Wendy, 2005]. The WHO Provisional Maximal Tolerable Daily Intake (PMTDI) (WHO, 2018) for Zn is set at 0.3 mg/kg/bw/day. In this present study, the estimated daily intake of Zn for adults and children ranges from 0.062-0.0216mg/kg/day and 0.034-0.118 mg/kg/day respectively. These values were far lower than the recommended daily intake.

The presence of chromium in diet is of great significance owing to its active influence in lipid metabolism and insulin function. The EDIs for chromium in this study spanned between 0.019-0.032 mg/kg/day for adults and 0.010-0.018 mg/kg/day for children. The Expert Group on Vitamins and Minerals (EVM) safe upper level for trivalent chromium is 0.15 mg/kg/day (EVM, 2013) and EDI in this study for Cr were below this recommended value. Lead is of no importance in the human body and can cause severe health problems particularly for children and pregnant women. It affects the behavior of children and also impairs performance in IQ tests.

The estimated daily intake of Pb in this study ranges from 0.004-0.010 mg/kg/day for adults and 0.002-0.005 mg/kg/day for children. The values in this study for adults exceeds Joint Expert committee on food and additives (JECFA) provisional tolerable intake which is 0.0036mg/kg/day while in children, only *ananas comosus* and *corchorus olitorius* (0.002 mg/kg/day) were estimated lower than the recommended value. Iron dietary daily intake in this study ranges from 0.154-0.287 mg/kg/day for adults and 0.084-0.157 mg/kg/day for children. These results obtained were below the tolerable daily intake value of 0.8 mg/kg/day recommended by scientific committee on food (SCF), 2003.

The EDIs for Cu in this present study ranges from 0.284-0.426 mg/kg//day for adults and 0.155-0.233 mg/kg/day for children and were also below the tolerable daily intake of 3 mg/kg/day given by FAO/WHO, 2010. Nickel recommended tolerable daily intake value given by European food safety authority (EFSA), 2015 was 0.0028 mg/kg/day whereas the EDIs values in this study exceeds the recommended value. The estimated target hazard quotient (THQ) of metal through the consumption of the food crops, fruit and vegetables from the study site for both adults and children were given in Table 5. The highest THQ was 33.3 in *manihot esculenta* (cassava) observed in adults. It must be known that the THQ values does not offer a quantitative evaluation of the possibility of an exposed population facing a reverse health effects, but rather they function as a suggestion of the risk level due to metal exposure.

THQ is usually used to determine the level of health risk following the consumption of such food items. It also used to indicate the level at which serious health effect could be manifesting. At values less than or equal to 1, is an indication of no adverse effect. This is the case with toxic metals Zn, Fe, Mn and Ni in the studied samples with THQ < 1. Except for *Amaranths spp with* THQ 1.3, all other food samples studied has quotient values les than 1. The THQ values for Pb in all the samples were however higher than 1, an indication of high risk in consumption of the food samples with respect to Pb metal

Table 4: Estimated Daily Intake (EDI) (mg/kg/day)of Fruits and Food Crops in the Study Area

Food crops & fruit	Category	Cd	Cr	Fe	Zn	Pb	Cu	Mn	Ni	As
Dioscorea alata (Water yam)	Adults	0.018	0.027	0.247	0.204	0.006	0.339	0.012	0.012	0.006
	Children	0.010	0.014	0.135	0.111	0.003	0.185	0.007	0.007	0.003
Colocasia esculenta (Cocoyam)	Adults	0.020	0.025	0.244	0.185	0.005	0.426	0.019	0.017	0.005
	Children	0.011	0.013	0.133	0.101	0.003	0.233	0.010	0.009	0.003
Manihot esculenta (Cassava)	Adults	0.023	0.027	0.256	0.191	0.006	0.389	0.016	0.015	0.010
	Children	0.012	0.015	0.140	0.105	0.003	0.212	0.009	0.008	0.006
Musa paradisiaca (Plantain)	Adults	0.022	0.030	0.262	0.216	0.010	0.410	0.020	0.019	0.008
	Children	0.012	0.016	0.143	0.118	0.005	0.224	0.011	0.010	0.005
Ananas comosus (pineapple)	Adults	0.011	0.020	0.287	0.142	0.004	0.346	0.017	0.015	0.004
	Children	0.006	0.011	0.157	0.078	0.002	0.189	0.009	0.008	0.002
Thaumatococcus daniellii (eweeran)	Adults	0.011	0.020	0.207	0.096	0.009	0.367	0.015	0.012	0.006
	Children	0.006	0.018	0.121	0.042	0.003	0.162	0.006	0.006	0.002
Senecio biafrae (woorowo)	Adults	0.012	0.032	0.222	0.077	0.005	0.296	0.012	0.011	0.004
	Children	0.007	0.010	0.084	0.034	0.004	0.155	0.008	0.006	0.001
Corchorus olitorius (ewedu)	Adults	0.012	0.019	0.154	0.062	0.007	0.284	0.015	0.011	0.001
	Children	0.009	0.010	0.101	0.057	0.002	0.196	0.013	0.007	0.002
Amaranthus hybridus (tete)	Adults	0.016	0.019	0.185	0.105	0.004	0.358	0.023	0.013	0.004
	Children	0.006	0.011	0.113	0.052	0.005	0.201	0.008	0.007	0.004
Daily Intake Limits (DLI)		NA	0.150[a]	0.800[b]	0.300[c]	0.0036[d]	3.000[e]	2.0[*], 11.0[**]	0.0028[f]	NA

Note: NA (not available), NRCC for [*] Children and [**]for Adults, [a] Expert Group on Vitamins and Minerals, [b] scientific committee on food, [c] WHO/PMTDI, [d] Joint Expert committee on food and additives, [e] FAO/WHO, [f] European food safety authority

Table 5: Estimated Targeted Hazard Quotient (THQ) of Heavy Metals for Adults and Children.

Food crops, fruit and vegetables	Category	Cd	Cr	Fe	Zn	Pb	Cu	Mn	Ni	As
Dioscorea alata (Water yam)	Adults	18.0	9.0	0.4	0.7	1.5	8.5	0.1	0.6	20.0
	Children	10.0	4.7	0.2	0.4	0.8	4.6	0.1	0.4	10.0
Colocasia esculenta (Cocoyam)	Adults	20.0	8.3	0.3	0.6	1.3	10.7	0.1	0.9	16.7
	Children	11.0	4.3	0.2	0.3	0.8	5.8	0.1	0.5	10.0
Manihot esculenta (Cassava)	Adults	23.0	9.0	0.4	0.6	1.5	9.7	0.1	0.8	33.3
	Children	12.0	5.0	0.2	0.4	0.8	5.3	0.1	0.4	20.0
Musa paradisiaca (Plantain)	Adults	22.0	10.0	0.4	0.7	2.5	10.3	0.1	1.0	26.7
	Children	12.0	5.3	0.2	0.4	1.3	5.6	0.1	0.5	16.7
Ananas comosus (pineapple)	Adults	11.0	6.7	0.4	0.5	1.0	8.7	0.1	0.8	13.3
	Children	6.0	3.7	0.2	0.3	0.5	4.7	0.1	0.4	6.7
Thaumatococcus daniellii (ewe eran)	Adults	11.0	6.7	0.3	0.3	2.3	9.2	0.1	0.6	20.0
	Children	6.0	6.0	0.2	0.1	0.8	4.1	0.0	0.3	6.7
Senecio biafrae (woorowo)	Adults	12.0	10.7	0.3	0.3	1.3	7.4	0.1	0.6	13.3
	Children	7.0	3.3	0.1	0.1	1.0	3.9	0.1	0.3	3.3
Corchorus olitorius (ewedu)	Adults	12.0	6.3	0.2	0.2	1.8	7.1	0.1	0.6	3.3
	Children	9.0	3.3	0.1	0.2	0.5	4.9	0.1	0.4	6.7
Amaranthus hybridus (tete)	Adults	16.0	6.3	0.3	0.4	1.0	9.0	0.2	0.7	13.3
	Children	6.0	3.7	0.2	0.2	1.3	5.0	0.1	0.4	13.3

Radionuclide Concentration and Hazard Risks in Fruit and Vegetable from Mining Site

The results of activity concentrations in the food, fruit and vegetable samples for natural radionuclides such as ^{238}U, ^{232}Th and ^{40}K were given in Table 6. The Table revealed generally high values for the concentration of ^{40}K in all the samples while they were all equally low in values recorded for Thorium-232. ^{40}K is an essential biological element and its concentration in human tissue is under close metabolic control and its high concentration observed in all the food samples from the study area is primarily due to the essential nature of potassium metal as plants do not have the capacity to separate or select between the different isotopes of the metal [Appiah et al, 2012]. The high ^{40}K might also be explained by the high content of clay and feldspar minerals that are very rich in the soil upon which the plant materials grow and derive their nutrient [Makinde et al, 2018]. The high value recorded for the radionuclide could as well be as a result of mans' activities such as mining, fertilizer and manure application on farm land and variation in the geological structure of the mining area [Adu-Yeboah and Obiri-Yeboah, 2008].

The highest concentrations displayed (Fig. iii) of ^{40}K (100.122±0.054 Bq/kg) was recorded in *Manihot esculenta (Cassava)* sample while the lowest concentration was 54.300±0.03 Bq/kg, found in plantain. The highest concentration of ^{238}U*was recorded in* Cassava sample *(Manihot esculenta)* at 18.119±0.031 Bq/kg, while the lowest value of the radionuclide (7.930±0.015 Bq/kg) was measured in *Ananas comosus (pineapple)* sample. The highest concentration of ^{232}Th 3.112 ± 0.005 Bq/kg was measured in *Manihot esculenta (Cassava)* sample. The lowest concentration of ^{232}Th 1.224 ± 0.011 Bq/kg was measured in *Ananas comosus (pineapple)* sample. These high values are not unconnected with the degree of illegal Gold mining operations extensively being carried out in the studied area.

Table 6. Concentration (Bq/kg) of ^{238}U, ^{232}Th and ^{40}K in collected Food samples

Samples	U-238 (Bq/kg)	Th-232 (Bq/kg)	K-40 (Bq/kg)
Thaumatococcus daniellii (ewe eran)	-	2.106 ± 0.18	58.772 ± 0.4
Colocasia esculenta (Cocoyam)	11.019 ± 0.02	1.416 ±0.021	77.892 ± 0.45
Corchorus olitorius (ewedu)	14.439 ±0.028	1.918 ± 0.017	78.542 ± 0.05
Ananas comosus (pineapple)	7.930 ±0.015	1.224 ± 0.011	57.922 ± 0.04
Musa paradisiaca (Plantain)	14.593 ± 0.028	2.33±0.02	54.300 ± 0.03
Amaranthus hybridus (tete)	11.900 ± 0.023	1.418 ±0.012	65.116 ± 0.04
Senecio biafrae (woorowo)	15.068 ±0.29	1.3209 ±0.012	89.560 ±0.07
Dioscorea alata (Water yam)	10.118±0.22	2.110±0.17	64.55±0.07
Manihot esculenta (Cassava)	18.119±0.031	3.112±0.005	100.122±0.054

Table 7: Risk Assessment indices of Food Crops, Vegetables and Fruit from the Study Area.

Samples	AGDR (D nGy/h)	AEDE (mSv/y)	AGDE (μSv/y)	ELCR
Thaumatococcus daniellii (ewe eran)	3.682	0.005	27.257	0.014
Ananas comosus (pineapple)	6.778	0.008	47.808	0.022
Dioscorea alata (Water yam)	8.596	0.011	60.353	0.030
Amaranthus hybridus (tete)	9.024	0.011	63.145	0.030
Colocasia esculenta (Cocoyam)	9.140	0.011	64.426	0.030
Musa paradisiaca (Plantain)	10.376	0.013	71.882	0.035
Corchorus olitorius (ewedu)	11.050	0.014	77.296	0.038
Senecio biafrae (woorowo)	11.431	0.014	80.203	0.038
Manihot esculenta (Cassava)	14.355	0.018	100.431	0.049
LIMIT	30-70***	1.0**	70.0****	0.29×10^{-3}*

The long-term exposure to Uranium through inhalation has several health effects, such as chronic lung disease, acute leucopenia, anemia and necrosis of the mouth. Uranium causes bone, cranial and nasal tumors. Thorium exposure can cause lung, pancreas, hepatic, bone and kidney cancers and leukemia. Therefore, gamma dose rates and other health risks (Table 7) associated with radionuclide activity concentrations should be monitored particularly in areas that are rich in uranium and thorium. The absorbed gamma dose rate (Table 7) ranges from (3.682 – 14.355) nGy/h. the lowest value was obtained in *thaumatococcus daniellii* and the highest value was obtained in *manihot esculenta*. The calculated values were compared with the data presented in UNSCEAR, 1988. The data presented in the UNSCEAR, 1988 report on selected countries of the world showed the gamma radiation dose rate ranging from 30-70 (nGy/h). The calculated values indicate that the dose of gamma radiation on the investigated area is in the range of doses reported in UNSCEAR, 1988.

The annual effective dose equivalent is the amount of gamma radiation released by a radioactive source which takes into account the radio- sensitivity of different organs of the human body. Calculated values of absorbed gamma dose were used to calculate the annual effective dose equivalent (mSv/y). The value ranges from (0.005-0.018) mSv/y with *thaumatococcus danielli* having the lowest value and *manihot esculenta* having the highest value. However, the measured values are below the limit set by CPR, 1991. The annual gonadal dose equivalent gives an estimation of the annual equivalent dose received in the gonads (reproductive organ). Calculated values of AGDE ranges from (27.257- 100.431) µSv/y with *thaumatococcus daniellii* having the lowest value and *manihot esculenta* having the highest value.

Table 7 showed 5 samples; *thaumatococcus daniellii* (27.257 µSv/y), *ananas comosus* (47.808 µSv/y), *dioscorea alata* (60.353 µSv/y), *amaranthus hybridus* (63.145 µSv/y) and *colocasia esculenta* (64.426 µSv/y) were below the limit 70 uSv/y given by Orgun et al.,2007 for AGDE while four samples; *musa paradisiaca* (71.882 µSv/y), *corchorus olitorius* (77.296 µSv/y), *senecio biafrae* (80.203 µSv/y) and *manihot esculenta* (100.431 uSv/y) exceeds the limit 70 µSv/y given by Orgun et al., 2007. The result obtained for *musa paradisiaca* is similar to the previous result obtained in the research journal by Makinde et al., 2016 who worked on *musa paradisiaca* leave. Consumption of the food samples that exceeds the limit can cause damage to the reproductive organ. It can also result in leukemia.

The carcinogenic effects of gamma radiation due to ingestion, inhalation and external exposure to a radioactive source are characterized by an estimation of cancer occurring probability during a specific lifetime. This probability is determined by the calculation of the excess lifetime cancer risk. The measured values for ELCR in Table 7 ranges from (0.014- 0.049) and it all exceeds the limit 0.29×10^{-3} as reported in UNSCEAR, 2000 (Fig iv). This estimation clearly showed that consumption of the food crops, vegetables and fruit in the study area is not safe and might pose a health issue to the populace due the effect of gamma radiation.

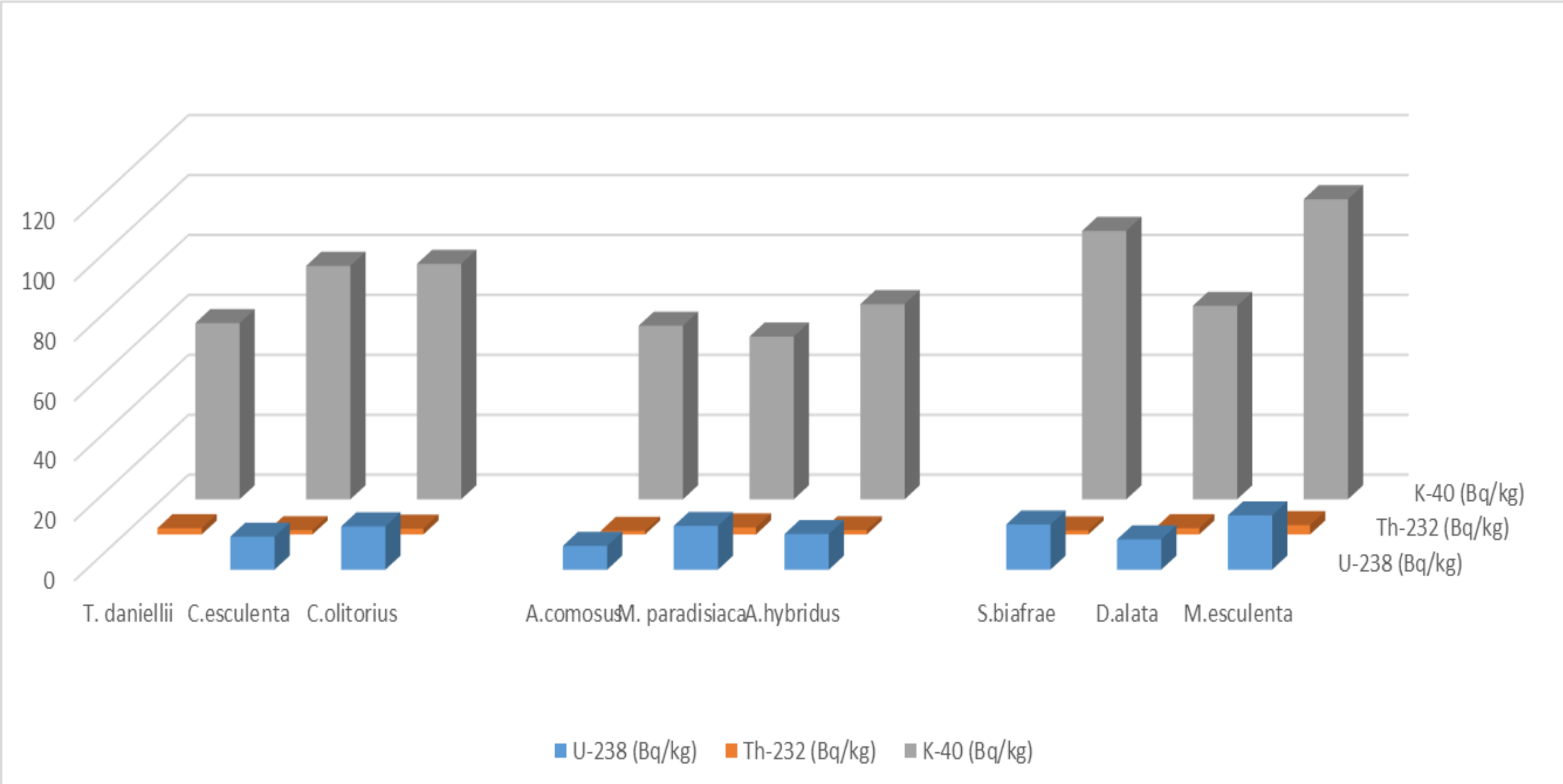

Figure ii. Concentration of Radionuclide in Food Crops, Vegetables and Fruits from the Study Area.

CONCLUSION

The concentration of heavy metals in the food crops, vegetables and fruit were mostly high with Cd, Cr, Cu, and As at values higher than permissible limits in all the samples. These significantly high concentrations call for caution in the consumption of the food materials since, for example, high level of Cr metal can cause hyperglycemia. All other metals observed in the samples were at concentrations below the permissible limit. The estimated daily intake of these food crops, vegetables and fruit showed that the intake of the toxic metals Pb, Cd, Ni and As in the studied samples were above provisional tolerable daily intake limits while recommended daily intake values for the essential metals: Zn, Fe, Cu, Mn, were within tolerable daily intake limits. The results obtained from AGDE in this present study suggest that *musa paradisca, corchorus olitorius*, *senecio biafrea* and *manihot esculenta* are more contaminated with radiations than any other samples studied, this could be an indication of high leukemia exposure and reproductive organ damage. Excess lifetime cancer risk (ELCR) showed that there is probability of cancer occurring at a specific lifetime as a result of the effect of gamma radiation on the food samples. Estimation of THQ showed that there is possible health effect related with chronic exposure to Pb, Cd, Cr and As indicating potential health concern for both adults and children who consume these food crops, vegetables and fruit on a regular basis. It is of no doubt that the contamination of these food items originated from mining activities in the study area and also the use of herbicides since the area is mainly for farming activities since high concentration of the metals observed in the control samples can be traced to the use of herbicides during farming activities. However, this demands for urgent need to impose strict regulations against illegal mining on farm lands and also impose strict quality control techniques during the process of production of herbicides to decrease the concentration of toxic metals to acceptable level for use on farmlands.

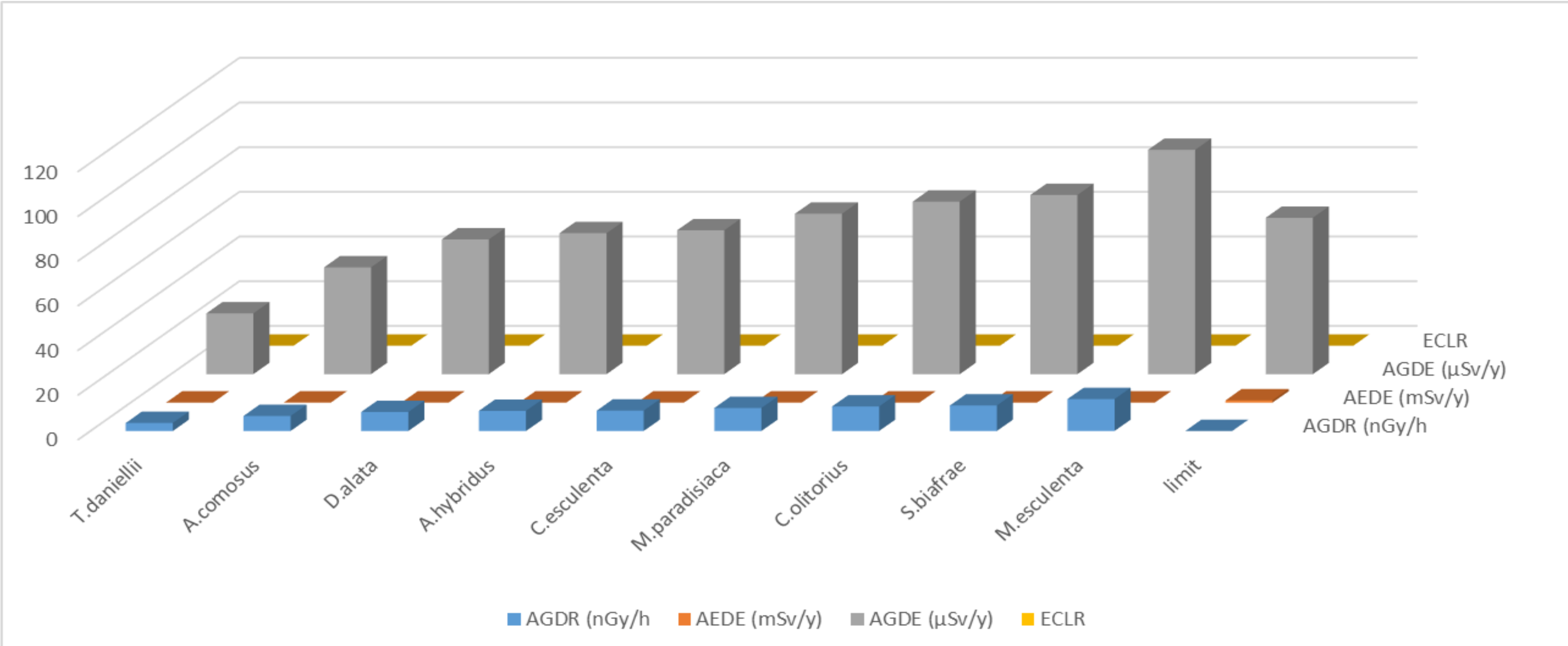

Figure iii. Hazard Risk Assessment.

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