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Research Article

Risk Assessment of Heavy Metals and Radionuclides in Vegetable Samples from Selected Nigerian Radiological Centers

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Abstract

In this study, the heavy metal and radionuclide contents of vegetable samples from some selected radiological centres have been determined using Energy Dispersive X-ray Fluorescence Analyzer and Gamma Spectrometer respectively. For heavy metals in vegetable samples from the three different sites, the mean concentration ranged from 0.680 to 8260.637 mg / kg. The results showed that the levels of Ti, Mn, Fe, Co, Zn, Br and Ca were relatively higher ($t > 0.05$) in the sites than control. In most cases, samples at the sites were slightly enriched in Mo, Zn, As, Se, Fe, Rb, Ti, (E.F = 1.100 - 9.00) but highly enriched in Br (EF > 10). For the radionuclides ^{238}U, ^{232}Th and ^{40}K, the absorbed dose rate in the samples ranged from (1.05 - 54.95) Bq/kg, (50.25 - 61.05) Bq/kg and (113.60 - 14560.56) Bq / kg respectively. The activity concentrations were higher than United Nations Scientific Committee on the Effects of Atomic Radiation guidelines for ^{232}Th and ^{40}K but lower for ^{238}U. The absorbed dose rates and annual effective dose were found to be in range of 50.400 to 120.900 (nGyh^{-1}) and 0.061 to 0.571 (μSvy^{-1}) respectively. The overall annual effective dose was lower than the allowable limit of 1mSvy^{-1} set by International Commission on Radiological Protection. H_{ex} and H_{in} were calculated and found to be within internationally recommended values. Findings from this study revealed that the vegetables from these sites were contaminated and are not good for consumption.

Keywords: *Risk assessment, Heavy metal and radionuclide Content, EDXRF, Gamma Spectrometer, Absorbed Dose rate.*

Introduction

Vegetables are rich in vitamins, carotenoids, minerals, dietary fiber and ascorbic acid. However, they can become contaminated when radioactive substances in form of vapor, liquid or solids are deposited on the surface of the leaf or uptake through the root system during growth. Radioactive substances can then pass from contaminated vegetation to grazing animals and humans that ingest either the plant or the animals. For instance, radioiodine fallout is absorbed by vegetables around radiology centres which is then consumed by cows, transmitted to milk and then drunk by humans. Radioactive contaminations or substances often contain a mix of radioactive isotopes, and sometimes associated with other contaminants such as solvents, pesticides, herbicides, petroleum hydrocarbons, and heavy metals. Heavy metals are non-biodegradable that has long biological half lives and also they are hazardous contaminants found in food and environment. They are also metallic elements that have relatively high density compared to water. Heavy metals are also considered as a

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trace element because of their presence is very low (ppb range to less than 10 ppm).

Heavy metals are easily accumulated in edible parts of leafy vegetables in quantities high enough to cause clinical problems both to animals and human beings when they are consumed; most of them are known to be potential carcinogens. Metals commonly found as contaminants in vegetables are As (Arsenic), Cd (Cadmium), Pb (Lead), which takes part as a significant health risks to humans especially when the concentrations are above the very low body requirements (Prabhat, 2019). All these together with the properties of the vegetables can affect the bioavailability of radionuclide in plants which is influenced by three factors: the physical factors such as temperature, phase association, sequestration, and absorption, biological factors such as biochemical or physiological adaptation and the chemical factors also influence separation at thermodynamic equilibrium and lipid solubility (Nagajyoti. *et al.,* 2010).

All these play an important role in exerting biochemical and physiological functions in plants and animals, which leads to unwanted side effects when these vegetables take up these heavy metals by absorbing them through airborne deposits on the parts of the plant that is exposed to the air from the polluted environment. The chemistry of heavy metals is a major contribution to their effects within the human ecological context. But in terms of usefulness, the world at large has been blessed by the abundance of heavy metals and the roles they play in balancing the ecosystem functions. Zn plays a crucial role in Dermatology; Cu is effectively used in treatment of radiation sickness and fish diseases. However, accumulation and bioaugmentation of these metals can adversely affects lives in the ecosystem with the opinion that most heavy metals are toxic even at low concentration of about 0.1 to 0.3 mg/l. Although some radioactive substances occur naturally in the environment, while some occur because of a release of radioactive material into the environment through human activities such as nuclear energy use and medical applications using X-rays, CT scans. Radiation is any energy that comes from a source and travels through space, such as light or heat. Unlike lights X-rays can penetrate through the body which makes it possible to produce images of internal body structures (Ugonna. *et al.,* 2020).

Man-made X-rays was first discovered by a German named Roentgen in 1895. In France, a year later, natural radioactivity was first identified with uranium by Becquerel. There are three kinds of radioactive elements from invisible rays are - alpha, beta, and gamma. Alpha particles are positively charged and they consist of two protons and two neutrons from the atom's nucleus. Alpha particles were first described in the investigations of radioactivity by Ernest Rutherford in 1899, and by 1907 they were identified as He^{2+} ions. Alpha particles are very energetic but they are heavy so they use up most of their energies over short distances and are unable to travel far and they come from the decay of the heaviest radioactive elements, such as Uranium, radium and polonium. Beta particle also known as Beta ray or beta radiation is a high energy that was accidentally found out while experimenting with florescence when uranium was exposed to a photographic plate enclosed with a black paper with some radiation that could not be turned off like x-rays. Beta particles are more penetrating than alpha particles, they are small, fast moving particles with a negative electrical charge that are emitted from an atom's nucleus during radioactive decay. A French chemist and physicist discovered gamma radiations in 1900 while studying radiation emitted by radium. In 1903, Ernest Rutherford named this radiation gamma rays based on their relatively strong penetration of matter. Gamma rays from radioactive decay are in energy range from a few kiloelectronvolts (keV) to approximately 8 meV, the energy spectrum of gamma rays can be used to identify the decaying radio nuclides using Gamma Spectroscopy. Natural sources of gamma rays originating on earth are mostly as a result of radioactive decay and secondary radiations from atmospheric interactions with cosmic ray particles. Gamma radiations from natural radionuclide and cosmic rays leads to external exposure while those obtained from inhalation and ingestion through foods leads to internal exposure to humans (IAEA in 1996) because they are ionizing radiations and thus biologically hazardous and due to their high penetration power and can damage the bone marrow and internal organs, this requires shielding made from dense materials such as lead or concrete, however there are other rare natural sources, such as terrestrial gamma ray flashes which produces gamma rays from electron from electron acting upon the nucleus. In 1996, IAEA (International Atomic Energy Agency) which is an international organization established as an autonomous organization on 29 July 1957, though was established independently of the United nations through its own international treaty, the IAEA Statute. They seek to promote the peaceful use of nuclear energy estimated that 20 % of doses contributions are from artificial radionuclide such as nuclear processes and medical purposes (X-rays) while 80 % are gotten from natural radionuclide containing potassium (^{40} K), thorium (^{232}Th), uranium (^{238}U) (IAEA 1996). Activities that produce radionuclides and heavy or toxic metals especially man-made activities have been in existence for years with little or no information about the effects associated with them. Vegetable is the major source of minerals, fiber, and vitamins and it is necessary because it plays an important role in human nutrition of the vast majority of people living in Ekiti state and Nigeria in general.

This research was undertaken to determine the levels of heavy metals and dose equivalent of vegetables around some selected radiological centers in Ekiti state with the aim to determining assess the risks of exposure to residents in these areas.

Material and Methods

Study Areas

The study areas were located at Ado-Ekiti town, Nigeria which lies within the latitude of 7.7 ° N and Longitude of 5.3 °E and Ido-Ekiti. It is a southwest region of Nigeria which was declared alongside five other states by the military government. In Ekiti, the wet season is warm, oppressive, and overcast and the dry season is hot, muggy, and partly hazy which is also referred to as a humid climate. Over the course of the year, the high temperature normally varies from 21° and 28 °C. Figure 1 shows the location map of the study areas.

Figure 1: Location map of the study area.

Sample Collection

Fifteen (15) vegetable samples were collected in all. Three (3) samples (each) of the species of each vegetable of the three species; *Talinum triangulare, Vernonia amygdaline*, and *Amaranthus cruentus*) from two radiological centers (Federal Medical Center Ido-Ekiti and Ekiti State Teaching Hospital Ado- Ekiti).

Identical samples were collected in an area far away from the sites but within the same location.

Sample Preparation

Samples which consisted of Bitter leaf and African spinach collected were weighed before drying. Freeze dryer machine was used to dry each sample was weighed 200 g. For Gamma spectrometric analysis, samples were further pulverized using an agate mortal and pestle. The crushed vegetables were sieved so as to get smooth and kept for more than twenty-eight days so as to reach secular equilibrium before analysis

Sample Analysis

Samples were analyzed for heavy metals using Energy Dispersive X-ray Fluorescence Spectrometer. Each sample was inserted into the sample holder of the XRF system for irradiation which is equipped with a silver (Ag) anode at a voltage of 25 kv and current of 50 micro amperes for 1000 counts or 17 minutes in an external chamber setup. The equipment model is PX 2CR Power supply and amplifier for XR-100 CR Si-pin detector. Characteristic X-ray of the sample was detected by the Solid-State SI-pin detector system and spectrum acquisition was done using an Amptek model multi-channel analyzer. While elemental analysis was done using the thick target mode of the International Atomic Energy Agency (IAEA) Quantitative Analysis of X-ray Iterative Least (Q-Axil) square software. The radionuclide content was also determined using Gamma spectrometer.

Determination of Activity Concentration (As) and Enrichment Factors

The activity concentrations of ^{238}U, ^{232}Th and ^{40}K were determined using this equation below.

$$A_S = \frac{N}{\varepsilon_f \ P_\gamma \ t_s \ m(Kg)}$$

Where N = the corrected net peak area of the corresponding full-energy peak

$N = N_S - N_B$

N_S = the net peak area in the spectrum of the sample
N_B = the corresponding net peak area in the background spectrum
ε_f = the efficiency at photo peak energy t_s = the live time of the sample spectrum collection in seconds
m = the mass (kg) of the measured sample
P_γ = the gamma-ray emission probability corresponding to the peak energy
K= the correction factor for nuclide decay from the time of sampling to counting
The absorbed dose rate (nGyh^{-1}) from the samples was calculated from the activity concentration of the relevant radio nuclide using the equation below (UNSCEAR, 2000).

$D\ (nGyh^{-1}) = 0.0417A_K + 0.462\ A_U + 0.604\ A_{Th}$ -------------------- (1) ---
Where Ak, Au, A Th are the activity concentrations of ^{40}K, ^{238}U, and ^{232}Th
The Annual Effective Dose rate
$AEDR\ (msv/yr) = D\ (nGyh^{-1}) \times (8760hy^{1}) \times 0.2 \times 0.7\ (svGy^{-1}) \times 10^{-6}$ ----------- (2)
Where D = dose rate 0.7 (svGy^{-1}) is a conversion factor.
AEDR (msv/yr) = $D \times 1.21 \times 10^{-3}$ for outdoor and $D \times 4.91 \times 10^{-3}$ for indoor.
The Radium Equivalent Dose rate (Ra_{eq}) in (Bq/kg)
$Ra_{eq} - Au + 1.43\ ATh + 0.077\ Ak$ (Beratka & Matthew, 1985) -------------- (3)

The external radiation hazard index (H_{ex}): The decay of naturally occurring radionuclide in vegetables produces an external radiation field to which all human beings are exposed. This was computed using the following equation and internal radiation index (H_{in}). (Krieger, 1981).

H_{ex} = Au/370 + A Th/259 + Ak/4810
H_{in} = Au/185 + A Th/259 + Ak/4810 ------------------- (4)

The annual effective dose (AED) is given by $\sum I_i \times 365 \times D_i$ in (µsv/yr) ----------- (5)
Where $I_!$ = daily intakes of radionuclide in (Bqd^{-1});
$D_!$ = ingestion dose co efficient ($SvBq^{-1}$).

The enrichment factor (EF) for each of the elements was determined by using crustal values and Fe as the reference element (Equation 1). Thus, Equation 1 indicates how enriched the samples are in heavy metals.

$$EF = \frac{X}{Conc\ of\ Fe(sample)} \Big/ \frac{Y}{Conc\ of\ Fe(\text{reference})} \qquad 1$$

Where X is the concentration of the element in the sample, Y is the concentration of the element in the reference. The reference used in this research is the non-contaminating site (i.e. the control).

Results and Discussion

The levels of heavy metals (mg/kg) in the three different vegetables observed in this study and control were presented in tables 1-3 (*Talinum triangulare,* bitter leaf and African spinach respectively). Table 4 gives the comparison of the results obtained in this study with WHO/FEPA limits while in table 5, the results obtained in this study were also compared with similar studies /literature review. Table 6 presents the t-test results while table 7 shows the degree of correlation of the levels of heavy metals in vegetables. The enrichment factors were calculated and table 6 presents the levels of enrichment of these elements in the three samples. Figure 1 shows the comparison of the calculated enrichment factors in the three different vegetables.

Table 1: Descriptive statistics of heavy metals in water leaf vegetable samples.

	Water leaf (*Talinum triangulare*) Site (mg/kg) n = 3		**Water leaf (*Talinum triangulare*) control (mg/kg) n = 3**	
Heavy Metal	**Mean ± S.D**	**Range**	**Mean ± S.D**	**Range**
K	7.048 ± 0.300	6.748 - 7.348	6.663 ± 0.857	5.806 - 7.520
Ca	8260.637 ± 636.294	7624.343 - 8896.931	7243.388 ± 29.471	6713.917 - 7772.859
Ti	66.847 ± 10.116	56.731 - 76.963	31.171 ± 9.172	21.999 - 40.343
V	12.528 ± 0.625	11.903 - 13.153	12.368 ± 0.326	12.042 - 12.694
Mn	27.771 ± 3.091	24.680 - 30.862	11.073 ± 1.489	9.584 - 12.562
Fe	111.615 ± 12.065	99.550 - 123.680	97.592 ± 1.472	96.120 - 99.064
Co	10.573 ± 0.649	9.924 - 11.222	9.574 ± 1.395	8.179 - 10.969
Ni	1.796 ± 0.217	1.579 - 2.031	1.552 ± 0.392	1.160 - 1.944
Cu	2.494 ± 0.109	2.385 - 2.603	2.499 ± 0.373	2.126 - 2.872
Zn	4.453 ± 0.433	4.020 - 4.886	3.478 ± 0.097	3.381 - 3.575
As	1.006 ± 0.001	1.005 - 1.007	0.650 ± 0.126	0.524 - 0.776
Se	1.196 ± 0.010	1.180 - 1.206	0.680 ± 0.006	0.674 - 0.686
Br	15.388 ± 1.676	13.712 - 17.064	0.950 ± 0.010	0.940 - 0.960
Rb	17.710 ± 4.473	13.237 - 22.183	5.730 ± 0.015	5.725 - 5.745
Mo	3.313 ± 0.430	2.883 - 3.743	2.207 ± 0.012	2.207 - 2.217

Table 2: Descriptive statistics of heavy metals in the bitter leaf vegetable samples

	Bitter-leaf (*Vernonia amygdalina*) Site (mg/kg) n = 3		**Bitter-leaf (*Vernonia amygdalina*) Control (mg/kg) n = 3**	
Heavy metal	**Mean ± SD**	**Range**	**Mean ± SD**	**Range**
K	3.934 ± 0.130	3.804 - 4.064	3.311 ± 0.291	3.020 - 3.602
Ca	7963.204 ± 127.011	7836.193 - 8090.215	1.733 ± 0.157	1.576 - 1.890
Ti	33.333 ± 7.224	26.109 - 40.557	26.667 ± 7.811	18.856 - 34.478
V	10.791 ± 0.420	10.371 - 11.210	9.982 ± 0.512	9.470 - 10.494
Mn	66.515 ± 0.825	65.690 - 67.340	16.926 ± 1.547	15.379 - 18.473
Fe	90.441 ± 1.537	88.904 - 91.978	48.267 ± 0.559	47.708 - 48.826
Co	8.418 ± 0.716	7.702 - 9.134	4.429 ± 0.642	3.787 - 5.071
Ni	2.553 ± 0.563	1.990 - 3.116	1.733 ± 0.272	1.461 - 2.005
Cu	5.990 ± 0.416	5.574 - 6.406	4.813 ± 0.195	4.618 - 5.008
Zn	10.038 ± 0.379	9.659 - 10.417	5.361 ± 0.156	5.205 - 5.517
As	1.621 ± 0.011	1.610 - 1.632	1.147 ± 0.239	0.908 - 1.386
Se	2.125 ± 0.012	2.113 - 2.137	0.930 ± 0.291	0.639 - 1.221
Br	8.199 ± 0.528	7.671 - 8.727	5.607 ± 1.176	4.431 - 6.783
Rb	36.225 ± 2.866	33.359 - 39.091	18.784 ± 0.512	18.272 - 19.296
Mo	3.270 ± 0.602	2.668 - 3.872	2.463 ± 0.010	2.453 - 0.473

Note: SD = Standard Deviation

Table 3: Descriptive statistics of heavy metals in the African spinach vegetable samples

Heavy Metals	**African Spinach (*Amaranthus cruentus*) Site (mg/kg) n = 3**		**African Spinach (*Amaranthus cruentus*) Control (mg/kg) n = 3**	
	Mean ± S.D	**Range**	**Mean ± S.D**	**Range**
K	3.784 ± 0.045	3.739 - 3.829	3.522 ± 0.277	3.245 - 3.799
Ca	3.561 ± 0.224	3.337 - 3.785	2.182 ± 0.030	2.152 - 2.212
Ti	136.757 ± 7.585	129.172 – 144.342	28.567 ± 1.321	27.246 - 29.888
V	25.193 ± 1.103	21.090 - 26.296	11.823 ± 0.156	11.667 - 11.979
Mn	31.674 ± 1.172	30.502 - 32.846	25.415 ± 2.418	22.997 - 27.833
Fe	168.899 ± 7.202	161.697 - 176.101	61.806 ± 1.533	60.273 - 63.339
Co	17.396 ± 0.945	16.451 - 18.341	6.547 ± 0.642	5.905 - 7.189
Ni	2.334 ± 0.570	1.764 - 2.904	2.215 ± 0.525	1.690 - 2.740
Cu	3.472 ± 0.294	3.178 - 3.766	3.335 ± 0.350	2.985 - 3.685
Zn	19.356 ± 0.400	18.956 - 19.756	9.530 ± 0.398	9.132 - 9.928
As	1.164 ± 0.010	1.154 - 1.174	0.951 ± 0.110	0.840 - 1.061
Se	2.399 ± 0.012	2.387 - 2.411	2.300 ± 0.578	1.722 - 2.878
Br	145.637 ± 1.807	143.830 - 147.444	5.923 ± 1.216	4.707 - 7.139
Rb	16.905 ± 3.203	13.702 - 20.108	15.564 ± 4.121	11.443 - 19.686
Mo	5.248 ± 0.605	4.643 - 5.853	1.878 ± 0.011	1.867 - 1.889

SD = Standard Deviation.

Table 4: Comparison of mean concentration of heavy metals in the vegetable Samples observed at the sites and control.

Heavy metal	**(*Talinum triangulare*) Site (mg/kg)**	**(*Talinum triangulare*) Control (mg/kg)**	**Bitter-leaf (*Vernonia amygdalina*) Site (mg/kg)**	**Bitter-leaf (*Vernonia amygdalina*) Control (mg/kg)**	**African Spinach (*Amaranthus cruentus*) Site (mg/kg)**	**African Spinach (*Amaranthus cruentus*) Control (mg/kg)**
K	7.048	6.663	3.938	3.311	3.784	3.522
Ca	8260.637	7243.388	7963.203	1.733	3.561	2.182
Ti	66.847	31.171	33.333	26.667	136.757	28.567
V	12.528	12.368	10.791	9.982	25.193	11.823
Mn	27.771	11.073	66.515	16.926	31.674	25.415
Fe	111.615	97.593	90.441	48.267	168.899	61.806
Co	10.573	9.574	8.418	4.429	17.396	6.547
Ni	1.796	1.552	2.553	1.733	2.334	2.215
Cu	2.494	2.499	5.990	4.813	3.472	3.335
Zn	4.453	3.478	10.038	5.361	19.356	9.530
As	1.006	0.650	1.621	1.147	1.164	0.951
Se	1.196	0.680	2.125	0.930	2.399	2.300
Br	15.388	0.950	8.199	5.607	145.637	5.923
Rb	17.710	5.730	36.225	18.784	16.905	15.564
Mo	3.313	2.207	3.270	2.463	5.248	1.878

Table 5: Comparison of the concentration of heavy metals in vegetable samples with WHO/FEPA Limits

Heavy metals	**(*Talinum triangulare*) Site (mg/kg)**	**Water leaf (*Talinum triangulare*) Control (mg/kg)**	**Bitter-leaf (*Vernonia amygdalina*) Site (mg/kg)**	**Bitter-leaf (*Vernonia amygdalina*) Control (mg/kg)**	**African Spinach (*Amaranthus cruentus*) Site (mg/kg)**	**African Spinach (*Amaranthus cruentus*) Control (mg/kg)**	**WHO/ FEPA Limits (mg/kg) (2011,2013)**
K	7.048	6.663	3.938	3.311	3.784	3.522	
Ca	8260.637	7243.388	7963.204	1.733	3.561	2.182	1000.000
Ti	66.847	31.171	33.333	26.667	136.757	28.567	1000.000
V	12.528	12.388	10.791	9.982	25.193	11.823	1000.000
Mn	27.771	11.073	66.515	16.926	31.674	25.415	6.640
Fe	111.615	97.593	90.441	48.267	168.899	61.806	420.000
Co	10.573	9.574	8.418	4.429	17.396	6.547	
Ni	1.805	1.552	2.553	1.733	2.334	2.215	10.000
Cu	2.494	2.499	5.990	4.813	3.472	3.335	40.000
Zn	4.453	3.478	10.038	5.361	19.356	9.530	60.000
As	1.006	0.650	1.621	1.147	1.164	0.951	1.400
Se	1.196	0.680	2.125	0.930	2.399	2.300	
Br	15.388	0.950	8.199	5.607	145.637	5.923	
Rb	17.710	5.730	36.225	18.784	16.905	15.564	
Mo	3.313	2.207	3.270	2.463	5.248	1.878	

Table 6: Comparison of some heavy metals in *Amaranthus cruentus* with Literature

Heavy metals	***Amaranthus cruentus*** **Uche (2019)**	***Amaranthus cruentus*** **Mohammed (2012)**	***Amaranthus cruentus*** **In this study**
Mn	26.300	33.920	31.674
Br	15.940	8.900	145.637
Ni	31.749	1.200	2.334
Zn	88.371	41.300	19.356
As	13.721	MDL	1.164
Cu	20.661	7.000	3.472
Fe	223.602	348.900	168.899
Cr	13.661	1.660	MDL

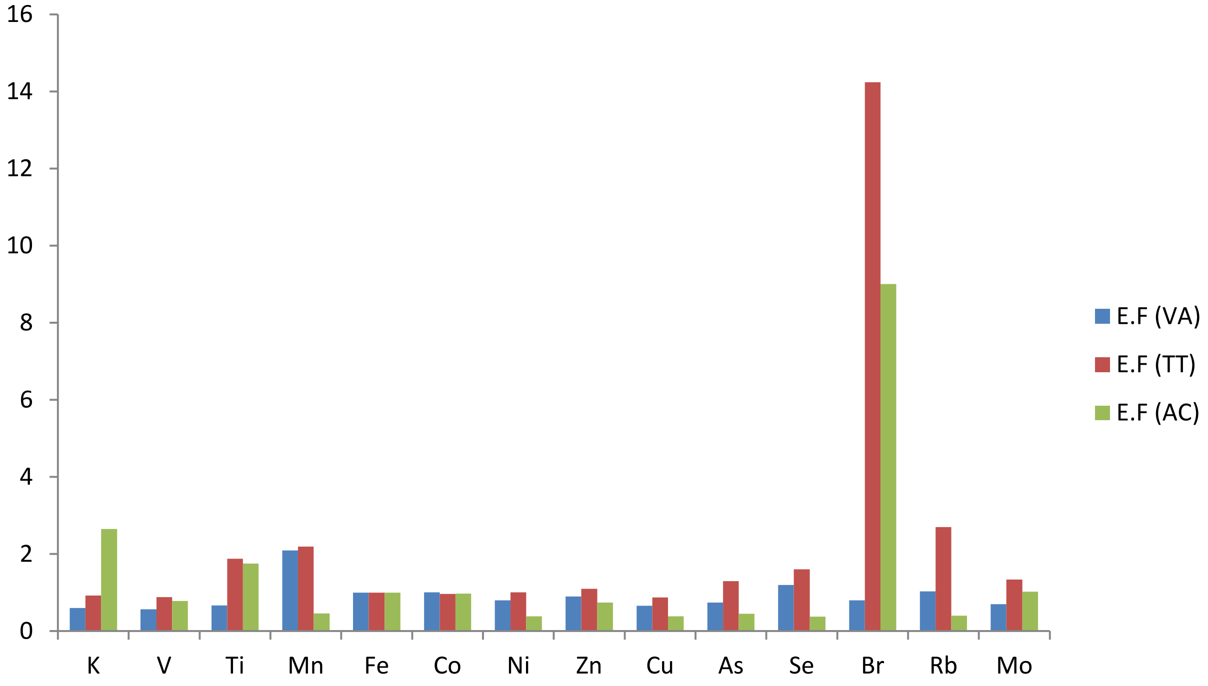

Figure 2: Comparison of the enrichment factors of heavy metals in the vegetable samples

Using Energy Dispersive X-ray Fluorescence Spectrometry, the results indicated that K, V, Ca, Ti, Mn, Fe, Co, Ni, Zn, Cu, As, Se, Br, Rb, and Mo in the sites were within 1.006 to 8260.637 mg/kg. In the sites, the mean concentration of Ca (mg/kg) was highest in water leaf followed by bitter leaf while African spinach had the lowest. This implies that different heavy metals have various rate of absorption by vegetables for Co, and Fe, African spinach had the highest concentration followed by water leaf and bitter leaf respectively. Using t-test, the levels of these heavy metals in the sites were relatively higher and significantly different (t values = 0.0001 to 0.0445) from control (for Fe, Co, Zn, Br, and Ca). The mean concentration (mg/kg) of Ca in Water leaf and Bitter leaf was higher than the permissible WHO/FEPA Limit. Mn in Water leaf, Bitter leaf and African spinach were also higher than the WHO/FEPA Limits. Arsenic (As) in bitter leaf was higher than WHO/FEPA Limit. Although Ca may not pose any health risks irrespective of its amount, but the reported high levels of Mn and As indicated that the vegetables at these sites were contaminated and their consumption can be detrimental to the health. However, continual exposure of the vegetables to these heavy metals could result in bioaccumulation and later become more toxic or not good for consumption. In most cases, the water leaf from the sites were slightly enriched in Ti, Ni, Fe, Mn, Zn, As, Se, Rb, Mo, and not enriched with K, V, Co, Cu, and Ca (Figure 2). The African spinach samples were slightly enriched with K, Ti, Fe, Br, Mo, and not enriched in Se, Rb, Ca, As, Zn, Cu, Ni, Co, Mn, V.

The radioactivity concentration of natural radionuclides ^{238}U, ^{40}K, Th^{232} in these vegetables were also measured using gamma spectrometry to assess the radiological risk in terms of hazard index. In vegetable samples, the results showed that the values of the activity concentrations (Bq/kg) ranged from 1163.60 to 1456.56, 50.25 to 61.05 and 1.05 to 54.95 for ^{40}K, ^{232}Th and ^{238}U respectively. This implied that the activity concentration of ^{40}K was relatively higher than Th^{232} and ^{238}U in the samples but below the global value of 500 Bq/kg by (UNSCEAR). Figure 3 gives the comparison of activity concentration of the three radionuclides in the vegetable samples.

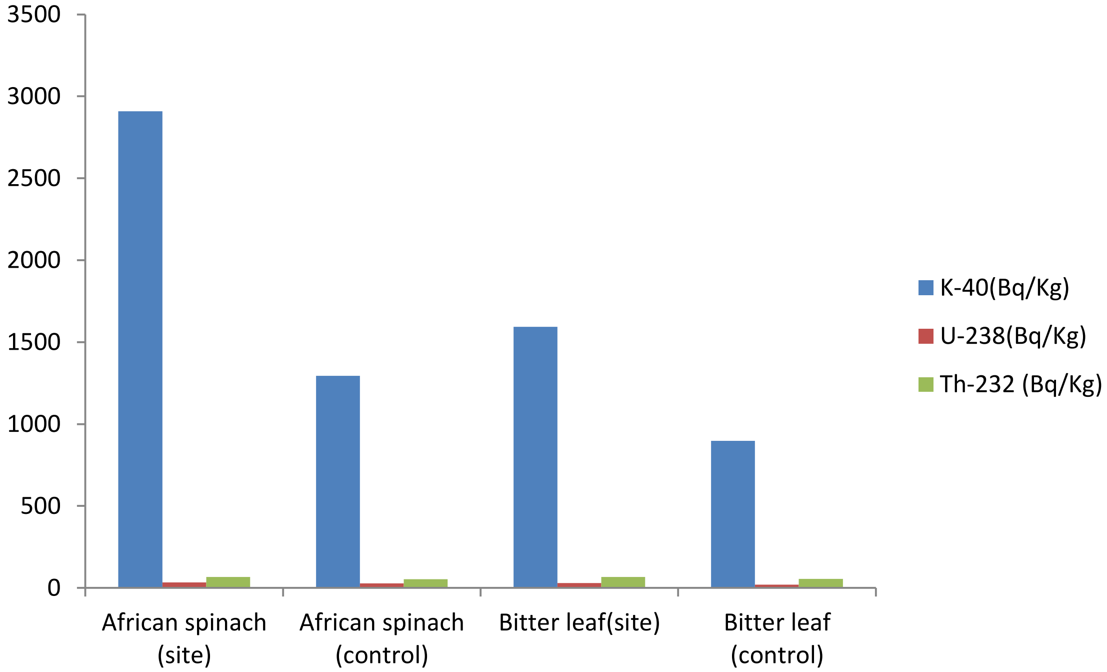

Figure 3: Activity Concentrations for ^{40}K, ^{238}U and ^{232}Th in the vegetable samples (Bq/kg)

The mean values of these naturally occurring radionuclides in vegetable samples were comparatively higher than their respectively control. The dose rate and the annual effective dose (nGy/hr), the Annual Effective Dose (outdoor and indoor, in (mSv/hr), the radium equivalent dose rate in (Ra_{eq}) in (Bq/Kg), external radiation hazard index (H_{ex}) and internal radiation hazard index (H_{in}) were also determined (Tables 7 and 8).

Table 7: Absorbed Dose rate, Annual Effective Dose rate of the vegetable samples

Sample	**Absorbed Dose Rate (nGy/hr)**	**Annual Effective Dose (mSv/hr) outdoor**	**Annual Effective Dose (mSv/hr) indoor**	**Radium Equivalent Dose (Ra_{eq}) (Bq/Kg)**	**Hex**	**Hin**
African spinach Site	116.300	0.141	0.571	240.500	0.650	0.741
African spinach control	50.400	0.061	0.248	203.500	0.550	0.627
Bitter leaf site	120.900	0.146	0.594	249.100	0.673	0.753
Bitter leaf Control	68.400	0.083	0.336	140.720	0.380	0.434

Table 8: Comparison of the activity concentration observed in this study with literature from different part of the world

U-238	Th-232	K-40	Country	Reference
28.00	55.65	1310.08	Nigeria	Present study
42.00	17.00	302.00	Cameroon	Adopted from (Mohammed. *et al*., 2012)
61- 72	-	-	India	Adopted from (Mohammed. *et al*., 2012)
24	18	-	USA	Adopted from (Mohammed. *et al*., 2012)
15.9	20.8	232	Nigeria	Adopted from (Mohammed. *et al*., 2012)
13.6	24.2	162.1	Ghana	(Faanu. *et al*., 2011)
35	30	420	World Average	(UNSCEAR, 2000)

The results obtained in this study were compared with published data from similar investigations in other parts of the country and the world permissible limits. Lower activity concentration was observed by (Faanu. *et al*., 2011) in Ghana (also a reference adopted from Mohammed (2012) in Nigeria). The average activity concentrations of ^{232} Th and ^{238}U were higher than the world average value and also higher than previous studies sited (table 8). The activity concentrations of ^{40}K were lower than the world permissible limit (UNSCEAR, 2000). This makes the vegetable unhealthy for consumption as it contains large amount of natural radionuclides which could be detrimental to health.

Conclusion

The levels of fifteen heavy metals (Sc, V, Ti, Fe, K, Ni, Cr, Rb, Ca, As, Se, Mn, Zn, Cu, Br) in three vegetable samples have been determined using Energy Dispersive X-ray Fluorescence spectrometry (EDXRF). The results obtained gave the baseline levels of these metals in vegetable samples from the selected radiological centres. Using t-test, the results showed that significant differences exist between some of the heavy metals in the sites and control ($t < 0.05$) while in few other heavy metals (such as As, V and Se), no significant differences exist ($t > 0.05$). In most cases the vegetables were slightly enriched in Fe, Ti, Rb, and Mn, but highly enriched in Br (E.F > 10). The relatively lower levels of most of these heavy metals compared with WHO/FEPA limits were an indication of little or no contamination by some heavy metals except Mn and Ca. The baseline concentrations of ^{238}U, ^{40}K, Th^{232} in vegetable samples as well as the dose rate in the study areas were established using gamma spectroscopy. The mean activity concentrations of ^{238}U, ^{40}K, Th^{232} in the vegetable samples were estimated to be 28.00, 1310.08 and 55.65 Bq/kg respectively. The results in this study area were in the range obtained by the similar studies carried out in different countries and with a worldwide average activity concentration (UNSCEAR, 2000). The potential exposure to the public in the study area was accessed by estimating the absorbed dose rate and annual effective dose rate in vegetables. The mean absorbed dose rate and the mean effective dose rates for the vegetables were found in the range of 89.00 nGy/hr and 0.12 mSv/hr. The absorbed dose rate obtained was higher than the worldwide mean value of 59 nGy/hr while the mean effective dose rate was lower than the recommended value by ICRP for (1mSv/year) for public radiation exposure. The results indicated significant levels of natural radionuclides and implied that the radiology activities pose radiological hazard to the communities in this area. Consequently, the radiological hazards (Ra_{eq}) to the population in the study area were assessed based on the calculation of radium equivalent activity (Ra_{eq}), hazard indices (external and internal) for vegetables. These were found to be less than the recommended maximum value (370 Bq/kg) and the external and internal hazard indices were less than unity. Hence, findings from the study revealed that the vegetables in such areas may not be good for consumption purpose and detrimental to the health.

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