Assessment of the Heavy Metal Concentrations in Selected Food/Plant Samples from Kano State, Nigeria Using the X-Ray Fluorescence Technique

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ABSTRACT

Heavy metals are natural components of the earth's crust; they are always present in the environment but anthropogenic activities often introduce them in larger quantities into the environment. Essential metals like Fe, Cu, Zn are needed for body growth and development. Others such as Pb, Cd e.t.c can cause adverse health effects when inhaled, ingested or absorbed. Therefore, the toxicities of heavy metals have gained public attention especially in developing countries. The aim of this research is therefore to determine the concentrations of heavy metals in some selected food and plant samples from Kano state, northern Nigeria. Thirteen (13) common food and plant samples were randomly collected from Dawanau and Yankura markets in Kano state. The samples were dried and ground to powdered form. X-ray fluorescence (XRF) technique was used for the analysis of the heavy metals. Each of the powdered samples was pelletized and placed in the sample holder for irradiation with x-rays of sufficient energy. The x-rays were generated in the Ag-anode tube operating at 25KV and 0.050mA. The sample holder was shielded in order to prevent exposure to the x-rays coming from the tube. The presence and concentrations of every element in the samples were detected by the XRF detector and were displayed by a read-out computer. Twenty heavy metals were detected in the samples. The concentration in the food samples ranged from <0.178 - 922.93 mg/kg while that of the plant samples ranged from 1.021 – 8853.84 mg/kg. The metal concentrations were compared with guidelines from WHO/FAO.

Keywords: heavy metals, x-ray fluorescence, earth's crust, detector, irradiation

INTRODUCTION

Cancer has become a leading health challenge facing humans. Although, its main cause and origin is still a bone of contention among many researchers, several agents have been identified as carcinogens. With the various on-going researches at international and local levels, studies have reported heavy metals as one of the human carcinogens. Heavy metals usually are metals with specific density >5 g/cm^3 and have ill effects on the lives of human, animals and the environment in general[1]. Due to advancement in science and technology and industrialization, environmental contamination and pollution by heavy metals have been on the increase, thus, posing a risk on the health of humans and animals. Hence, heavy metals among other pollutants have received a great deal of attention by environmental chemists, private and governmental bodies[2] .

Heavy metals such as copper, zinc, iron are needed for sustaining life. The others are highly poisonous and can induce oxidative stress, DNA damage, malignant growth and cell death in humans which lead to increase in the risk of cancer and cancer- related diseases[3,4]. Arsenic, cadmium, lead and mercury are listed among the ten chemicals of major public concern by WHO for their potential to be carcinogenic and to cause damages on organs and tissues of the body[4]. Heavy metals though toxic, are still being utilized in the industries for manufacturing and production activities. Hence, the presence and exposure of heavy metals cannot be completely wiped off from the environment since they originate from airborne particles, soil, water which then gets to foods[5] .

O.P. Sobukola *et al.* (2010)[6] investigated the concentrations of heavy metals in fruits and leafy vegetables from selected markets in Lagos, Nigeria using Atomic Absorption Spectrometry. Lead, cadmium, copper, zinc, cobalt and nickel were detected. The study reported the levels of cadmium and copper to be the lowest while the level of nickel and lead were the highest in the samples. Generally, the results were within the WHO/FAO safe limits with the exception of cadmium being higher in some samples. The study concluded that the vegetables and fruits gotten from the selected markets were safe for consumption.

Similarly, Oladebeye Abraham (2017)[7] assessed the heavy metals in Nigerian vegetables and soils in Owo and Edo axes using the XRF technique. He found that the concentrations of chromium (Cr), zinc (Zn), manganese (Mn), iron (Fe), and aluminium (Al) of the vegetable and soil samples collected from four (4) different local government areas were higher than the permissible limits of by WHO/FAO and EU for soils and plants in most of the samples.

The aim of this project is to assess the concentrations of heavy metals in some selected food and plant samples grown in Kano state of Nigeria using X-ray fluorescence (XRF) technique.

MATERIALS AND METHODS

Study Area

This study was carried out in Kano state. Kano state is one of the most prominent states in the northern region of Nigeria with approximate latitude and longitude 12.0022°N, 8.5920° E respectively. It is located at 481 meters (1580 feet) above sea level and covers a land area of approximately 20,760 square kilometer. It occupies a central position in Nigeria being the largest city after Lagos and Ibadan. Kano state consists of 1,754,200 hectares of agricultural land and over 92, 250, 81 hectares of forest vegetation and grazing land. Notable for its commercialization, industrialization and agriculture, Kano state is bounded on the west by Katsina state, on the south west by Kaduna state, on the east by Jigawa and Bauchi states and on the north by Niger Republic[8]. Kano state is among the sudano-sahelian zone of Nigeria.

Sampling locations

The samples were randomly collected from Dawanau and Yankura markets in Kano state. Dawanau market is the largest grain market not only in Nigeria but also in West Africa. Food items such as beans, soya beans, cassava, millet, sesame seed, hibiscus flower e.t.c are sold in this market to people within and outside Nigeria for direct consumption, wholesale and retail business.

Yankura is also a large market located at Ahmadu Bello way and deals with the sales of various consumer goods which include foodstuff.

Figure 1. Map of Nigeria showing the position of Kano state
(Adopted from Dawaki *et al.,2015*)[9]

Samples collection and preparation

Thirteen (13) common food samples: white rice, brown rice, wheat, millet, white corn, kuka (baobab leaf), white beans, soya beans, guinea corn, brown beans, ginger, karkashi (sesame seed), zogale (moringa leaf) were collected from Dawanau and Yankura markets in Kano state. The samples were handpicked in order to remove unwanted particles. The dried samples were taken to a grinding mill in Basorun, Ibadan and ground into fine powder. The powdered samples were labeled appropriately and then taken for XRF analysis.

Measurement Technique

The XRF system used for this work is located at the Centre for Energy Development and Research (CERD), OAU, Ile-Ife. It is a portable AMPTEK(R) Energy Dispersive X-ray Fluorescence (EDXRF) system. The EDXRF instrumentation includes; an x-ray source, sample holder, current and voltage amplifier and a read out computer.

Sample preparation was done by exposing the samples in the sample holder of the XRF system and was bombarded by X-ray fluorescence spectrometer with a silver (Ag) anode at a voltage of 25 kV and current of 50 μA for 1000 counts or 16 minutes in an external chamber setup. The equipment model is PX 2CR Power Supply and Amplifier for XR-100CR 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 Spectroscopy (QXAS) software.

When the sample absorbs an incoming x-ray photon with sufficient energy, the x-ray can expel an electron from the atom, leaving behind a hole in the shell. This leaves the atom in an excited state and thus becomes unstable. To make the excited atom reach stability, an electron from the outer shell comes to fill the hole (vacancy). For example, if an electron in the K shell is ejected from the atom by an incoming radiation, an electron from the L or M shell comes in to fill the vacancy. This is usually accompanied by the release of a secondary x-ray known as fluorescent x-ray whose energy is equal to the energy difference between the two quantum states of the electron. Therefore, XRF is a product of absorption and the fluorescent x-ray energy is the basis of XRF analysis.

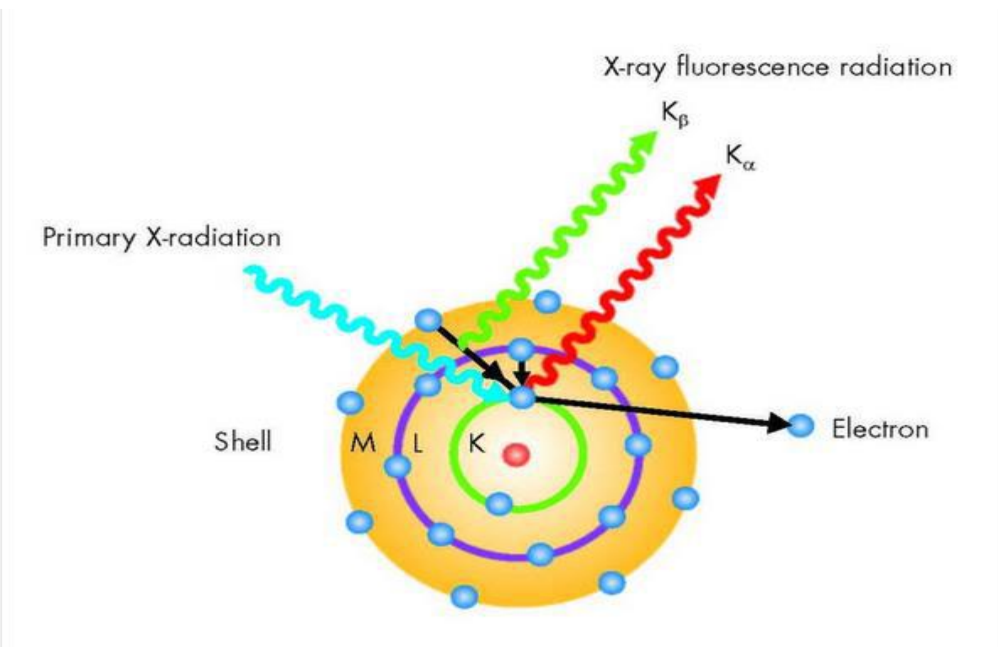

Fig 2. Picture explaining the principle of x-ray fluorescence spectrometry (Adopted from https://xrf-spectroscopy.com/)[10]

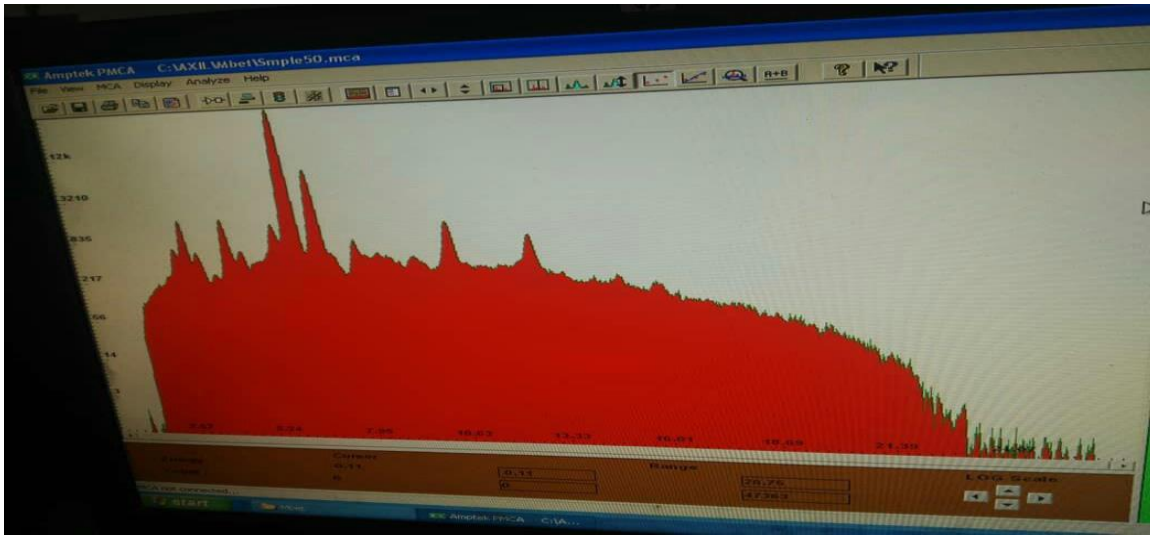

Fig 3. Typical spectrum of the XRF spectrometry showing the elements detected

RESULTS AND DISCUSSION

The results of the XRF elemental analysis according to their concentrations in parts per million (ppm) which is also known as milligram per kilogram (mg/kg) of the food/plant samples are given in Tables 1 and 2 below.

Table 1

Heavy metal concentrations of food samples from Dawanau and Yankura markets, Kano state

				Conc		(mg/kg)			
Metal	W.R	B.R	W.B	B.B	W.H	M.T	S.B	G.C	W.C
K	467.39	176.76	828.13	922.93	415.22	318.70	854.29	447.86	322.74
Ca	<65.36	13.58	100.12	106.25	<65.12	17.25	136.33	33.958	25.29
Mn	2.118	<1.800	<2.157	2.180	<1.861	<2.169	4.569	2.327	2.141
Fe	42.140	69.798	19.454	28.936	10.171	131.944	81.445	65.377	62.158
Co	<2.513	6.335	<1.369	<2.181	<1.253	14.433	9.103	7.134	<4.196
Ni	2.625	<1.174	1.991	2.568	2.093	<2.727	<2.065	<2.350	1.982
Cu	3.517	2.677	3.288	4.408	3.765	<2.323	<2.325	4.597	3.615
Zn	4.457	1.592	4.793	6.059	4.261	<3.786	<2.308	3.447	4.695
As	<1.174	<0.883	<0.789	<0.749	<1.033	<0.474	<0.649	0.822	<0.929
Rb	<0.320	<0.359	1.225	2.945	<1.243	1.131	<1.055	1.067	<1.012
Zr	<1.097	0.507	<1.158	<0.712	<0.462	1.116	<0.885	<0.581	<0.531
Mo	<1.296	<0.824	<1.071	<0.480	0.870	0.815	0.760	<0.462	<0.412
Ru	<1.429	<0.371	<0.332	<1.477	<1.112	<0.359	<0.950	<0.415	<1.327
Ag	<0.651	<0.178	<0.566	<0.622	<0.416	<0.416	<0.333	<0.238	<0.983
Cd	<0.320	<0.213	<0.302	0.675	<0.213	0.462	<0.320	<0.238	<0.320
In	0.733	0.687	<0.435	<0.412	0.458	<0.435	0.504	0.641	0.687

W.R = white rice M.T = millet B.R = brown rice S.B = soya beans W.B = white beans
G.C = guinea corn B.B= brown beans W.C = white corn W.H= wheat

Table 2
Heavy metal concentrations of plant samples from Dawanau and Yankura markets, Kano state

	Concentration in mg/kg			
Metal	Kuka	Ginger	Karkachi	Zogele
K	7039.861	3.323	8853.842	1.581
Ca	7804.729	1775.243	1.021	1.434
Sc	566.766	174.542	653.044	972.896
Ti	96.769	91.692	129.231	50.462
Mn	17.060	169.768	57.585	27.029
Fe	254.860	544.226	1936.349	825.257
Co	227.938	57.649	232.004	87.784
Ni	5.512	<6.558	<19.759	<9.328
Cu	8.833	<9.428	9.347	<9.891
Zn	8.647	<8.057	<8.595	<11.050
As	<1.598	<3.125	<3.864	<2.273
Rb	15.303	<15.866	<23.747	<8.634
Sr	119.087	<25.298	86.384	36.405
Zr	<53.826	<107.652	<192.604	<61.350
Nb	<117.269	<251.291	<454.115	<142.398
Mo	<320.460	739.523	<1403.147	895.645
Ru	ND	ND	ND	ND
Ag	<5.834	<11.667	<7.263	<16.845
In	ND	ND	ND	<298.955
Cd	<34.149	ND	<29.574	ND

ND= Not Detected

Table 3

International / National guidelines for some heavy metals in foods

Metals	mg/kg	Reference
Cu	30	[11]
Fe	48	[11]
Zn	99.4	[12]
Ni	0.2	[13]
Co	60	[14]
Cd	0.2	[11,15]
As	1.4	[16]
Mo	10	[14]

Health Risk Index (HRI) of Heavy Metals

The Health Risk Index (HRI) is used to evaluate the potential risk to human health from exposure to a particular heavy metal. It is often given as

$$HRI = \frac{DIM}{RFD} \ldots\ldots\ldots\ldots\ldots\ldots\ldots .(1)$$

Where DIM= Daily intake of metal= $\frac{C_{metal} \times C_{factor} \times D_{food\ intake}}{B_{average\ weight}}$

$$C_{metal} = concentration\ of\ heavy\ metal\ in\ plants\ in\ mg\ /\ kg$$

$$C_{factor} = conversion\ factor = 0.085$$

(Adopted from Khan *et al., 2009*)[17]

$$D_{food\ intake} = \text{daily intake of vegetable} = 0.345\ \text{kg/adult}\ person\ /\ day$$

RFD = Oral reference doses

An HRI > 1 suggests that there are significant health effects from the consumption of the heavy metal contaminated food items.

The available oral reference doses for some heavy metals are given in table 4

Table 4: Oral reference doses for some metals

Metal	Oral reference dose (mg/kg/day)
Cu	0.04
Fe	0.7
Zn	0.3
Ni	0.02
Cd	0.001
As	0.0003

(Adopted from Workineh, 2018)[18]

Using the expression in (1), the Health Risk Indices of the plant samples are calculated as follows;

Table 5: HRI of the plant samples

Sample	Cu	Fe	Zn	Ni	Cd	As
Kuka	0.11	0.18	0.01	0.13	6.43	2.60
Ginger	0.12	0.38	0.01	0.16	0	5.09
Karkachi	0.11	1.35	0.01	0.48	14.45	6.30
Zogele	0.12	0.58	0.01	0.23	0	3.70

CONCLUSION

The concentrations of heavy metals in selected food and plant samples from Dawanau and Yankura markets in Kano state have been studied using the X-ray fluorescence technique. The study revealed that the concentrations of Fe, Ni, Cd in both the food and plant samples exceeded the WHO/FAO permissible limits and the concentrations of As, Mo, Co were exceeded only in the plant samples. Heavy metals such as Pb, Mg, Cr which are considered most toxic were not detected in any of the samples.

Cadmium, Arsenic and Nickel detected in the samples are among the known toxic heavy metals in the world. The mean concentration of Cd in the food samples was 0.34 mg/kg and 31.8615 mg/kg in the plant samples. These exceeded the threshold value of 0.2 mg/kg by international/ national bodies. The mean concentration of As in the food samples is 0.833 mg/kg and 2.715 mg/kg. The threshold value of 1.4 mg/kg for As was only exceeded in the plant samples while both the food and plant samples exceeded the tolerable limit of 0.2 mg/kg for Cd. The permissible limit of 0.2 mg/kg for Ni was exceeded by all the samples.

Presently, there is not enough information about the biological roles of heavy metals such as Rb, Zr, Ru, In, Sc, Sr, Ti and Nb, so, they cannot be scientifically established as being toxic.

Generally, the concentrations of heavy metals in the plant samples are higher than that of the food samples. This could be because plants have higher abilities to absorb metals from the soil, air or water. Anthropogenic activities are the main reasons for the high concentrations of heavy metals in the samples. The Health Risk Indices (HRI) calculated for Cd and As in the plant samples ranged between 2.60 to 14.45. These values are far greater than one and suggest a dangerous health effects associated with their consumption.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interest.

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