

## HEALTH IMPLICATION AND NUTRITIONAL VALUE OF BAOBAB LEAVES IN KATSINA STATE, NIGERIA USING INSTRUMENTAL NEUTRON ACTIVATION ANALYSIS

Joseph, E.<sup>1\*</sup>, Lawal, A. U.<sup>1</sup>, Ubaidullah, A.<sup>2</sup> & Kado, S.<sup>1</sup>

<sup>1</sup>Department of Physics, Federal University of Dutsin-Ma, Katsina State, Nigeria.

<sup>2</sup>Department of Geophysics, Federal University of Dutsin-Ma, Katsina State, Nigeria.

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**Abstract:** Medicinal plant renders herbal remedies for human ailments and hence prevail over traditional healthcare practice. Baobab tree is an African tree with a long history in traditional and pharmaceutical properties and nutritional value. This study investigates the presence of heavy metals in baobab leaf samples in Katsina state using neutron activation analysis technique. Health risk associated with the consumption of baobab leaf was evaluated by estimating the daily heavy metals intake and target hazard quotient (THQ) for cancer and non-cancer risks. The study revealed that the mean concentration of some of the detected heavy metals ranged between  $16.0 \pm 0.1 - 37.5 \pm 0.2$  mg/kg for Br,  $0.021 - 0.068 \pm 0.011$  mg/kg for U,  $0.51 - 2.45 \pm 0.41$  mg/kg for Cr,  $506 \pm 66 - 1670 \pm 95$  mg/kg for Fe,  $0.28 \pm 0.04 - 3.49 \pm 0.12$  mg/kg for Co,  $53.9 \pm 0.3 - 442 \pm 1$  mg/kg for Mn, and  $1.58 \pm 0.18 - 10.8 \pm 2.6$  mg/kg for V, which are higher than the USEPA and WHO/FAO established tolerable limits, while those heavy metals that were found to be lower than the tolerable limits are found to range between  $0.086 - 0.30 \pm 0.05$  mg/kg for As,  $4.99 - 24.5 \pm 4.1$  mg/kg for Zn, and  $1.41 - 2.42$  mg/kg for Cu. Also, the risk level (THQ < 1) was observed for all the detected heavy metals for adults except for Mn in Daura, Fe in Funtua and Malumfashi, so also in children except for Mn in Daura, Funtua, Malumfashi, while the risk level (THQ > 1) was found in children in all the studied locations. Accordingly, except for adults in Kankia. Thus, it is deduced that, consumption of baobab leaves from Katsina state may pose a serious health risk and increase the level of cancer risk to the inhabitants

**Keywords:** Baobab Leave, Toxic Element, Instrumental Neutron Activation Analysis, Medicinal Plant

### 1. INTRODUCTION

The world is enriched with high abundance of medicinal plants which have long been utilized in traditional medicine and worldwide ethnomedicine, the herbs provide the starting material for the isolation or synthesis of conventional drugs (Michael *et al.*, 2015). Medicinal plants have curative properties due to the presence of various complex chemical substances of different composition, There is a growing interest in natural antioxidants, present in medicinal and dietary plants that might help attenuate oxidative damage (Silva *et al.*, 2005, Shakeri *et al.*, 2012). Many studies have reported that medicinal plants have great potential to treat different ailments including chronic diseases (Greenberger, 2003). These plant metabolites, according to their composition, are grouped as alkaloids, glycosides, corticosteroids, essential oils, among others (Michael *et al.*, 2015). The investigation of medicinal properties of various plants attracted an increasing interest since last couple of decades because of their potent pharmacological activities. Medicinal plants play an important role and main resource for new drug discovery and commonly the local practitioners are used to treat various diseases (Raju *et al.*, 2003).

Epidemiological studies have indicated that frequent consumption of natural antioxidant is associated with a lower risk of cardiovascular disease and cancer (Abdullah, 2009). Though many plants have been screened for antimicrobial properties, cytotoxicity, and antioxidant capacity with some leading to the discovery of the derived drugs known today, a vast majority of them have not yet been adequately evaluated. According to Mojeremane et al. (2004) and Petrea et al. (1999), the nutritional value of indigenous fruit bearing tree species indicate that many are

rich in sugar, essential vitamins and minerals while others are high in vegetable oil and proteins. It has also been documented that diet is the main source of trace element and the nutritional importance of many trace elements has been established (Joseph *et al.*, 2011)

Baobab Also known by their scientific name *Adansonia*, is a deciduous tree that are native to Africa, Australia, and the Middle East. The bark, seeds, fruits, and leaves of the baobab tree has been used as food and medicine. Baobab trees can grow up to 98 feet (30 meters) tall and produce a large fruit that is commonly consumed and appreciated for its delicious citrus-like flavor. In many parts of Africa, baobab leaves provide a reliable source of food for the rural population (Rabiu *et al.*, 2021). In the northern region of Nigeria and neighboring countries, the leaves are traditionally used to prepare soup (Gwana *et al.*, 2016). According to Bustwat *et al.* (1997), baobab leaves are a significant source of protein that can complement the amino acid profile and provide the dietary quality of protein. They are also a rich source of vitamins and minerals, such as calcium and vitamin C. The baobab tree is a versatile plant with several culinary and medical uses for its products, as well as a fibrous bark with a multitude of applications (Wickens, 1982; Codjia *et al.*, 2001; Sidibe and Williams, 2002). Baobab leaves are a great source of mineral components, whose significance in the human diet is undeniable, in addition to their high concentration of vitamin C and beta-carotene (Agbemaflé *et al.*, 2012; Joseph *et al.*, 2019).

Baobab is a fruit that has been associated with a number of impressive health benefits. In addition to supplying many important nutrients, adding baobab to your diet may aid weight loss, help balance blood sugar levels, reduce inflammation and optimize digestive health. Best of all, baobab at least in powdered form is easy to find and incredibly versatile, making it easy to add to your diet and enjoy. However, the potential health benefits of baobab leaves can never be overemphasized, Baobab leaves are highly nutritious and have been used traditionally in treating almost all kinds of diseases, such as Malaria, tuberculosis, anemia, dysentery, toothache, microbial infections, and fever. In Nigeria, baobab leaves are used to prepare a delicacy known as *miyan kuka*, it is a popular meal in Northern Nigeria. In 2009, the Baobab fruits were recognized as safe by the U.S. Food and Drug Administration (FDA). So, the leaves are equally safe to consume. Baobab leaves contain essential vitamins that work together to improve your overall physical health. According to a study, baobab leaves is rich in vitamin C which is an antioxidant that helps to fight infections by boosting your immune system. Vitamin C also prevents free radical damage caused by stress or pollution. The leaf contains vitamin K, which helps in blood clotting, and is necessary for the formation of bones. Vitamin K also regulates bone mineralization and bone metabolism and helps to prevent osteoporosis. The Vitamin B1 (thiamine) component of the baobab leaves helps in the formation of new cells, especially muscle cells. Also, it provides energy for brain function and heartbeat. The vitamin B2 (riboflavin) content in the leaf is essential for growth and reproduction as well as the normal functioning of the nervous system. Also, baobab leaves contain vitamin B3 (niacin) which contributes to the maintenance of healthy skin and mucous membranes as well as the normal functioning of the digestive system. Baobab leaves contain relevant minerals such as potassium and magnesium, both of which are important for bone health. Baobab leaves contain fiber that helps to promote digestion by regulating bowel movements and preventing constipation. The fiber content also lowers bad cholesterol levels in the blood while increasing good cholesterol levels, which ensures proper blood circulation throughout your body. In addition, baobab leaves are rich in antioxidants which help protect cells from free radical damage that can lead to cancer, heart disease, and premature aging. It also prevents certain types of cancers because it boosts the production of white blood cells that help fight infections before they become cancerous tumors in our bodies or spread to other organs or tissues. It is advised not to consume the leaves at their raw stage, as it might cause some allergies. Though most people can safely consume baobab, some potential side effects should be considered. First, the seeds and pulp contain anti-nutrients, such as phytates, tannins and oxalic acid that can reduce nutrient absorption and availability. However, the number of anti-nutrients found in baobab is too low to be of concern for most people, especially if you follow a well-balanced diet rich in other healthy whole foods.

The goal of this work is to estimate the presence of toxic and trace elements in baobab leaves from Katsina state, Nigeria using Instrumental Neutron Activation Analysis Technique., because baobab leaves have been proven to be a primary food source for the rural people in Katsina state. Certain heavy metals are present in leaves as contaminants and can only be identified chemically using the appropriate analytical techniques rather than by taste, smell, or sight (Rabiu *et al.*, 2021). And in INAA technique, the elements to be measured in any given sample were

made radioactive by irradiating the sample with neutrons. The number of detected gamma-rays of any particular energy is directly proportional to the disintegration rate of the radionuclide, which in turn also is directly proportional to the amount of parent isotope present in the sample (Joseph *et al.*, 2015)

## 2. MATERIALS AND METHOD

### 2.1 Study Area

Katsina state is situated between latitude 11°07'49" and 13°22'57" N and longitude 6°52'03" E and 9°9'02" E. According to the National Population Census of 2006, Katsina has land area of about 23,938 km<sup>2</sup> (9,243 Sq mi) and a population of 9,054,106. The average annual rainfall, temperature and relative humidity of the state are 1,312 mm, 27.3°C and 50.2% respectively (KSIH, 2016).

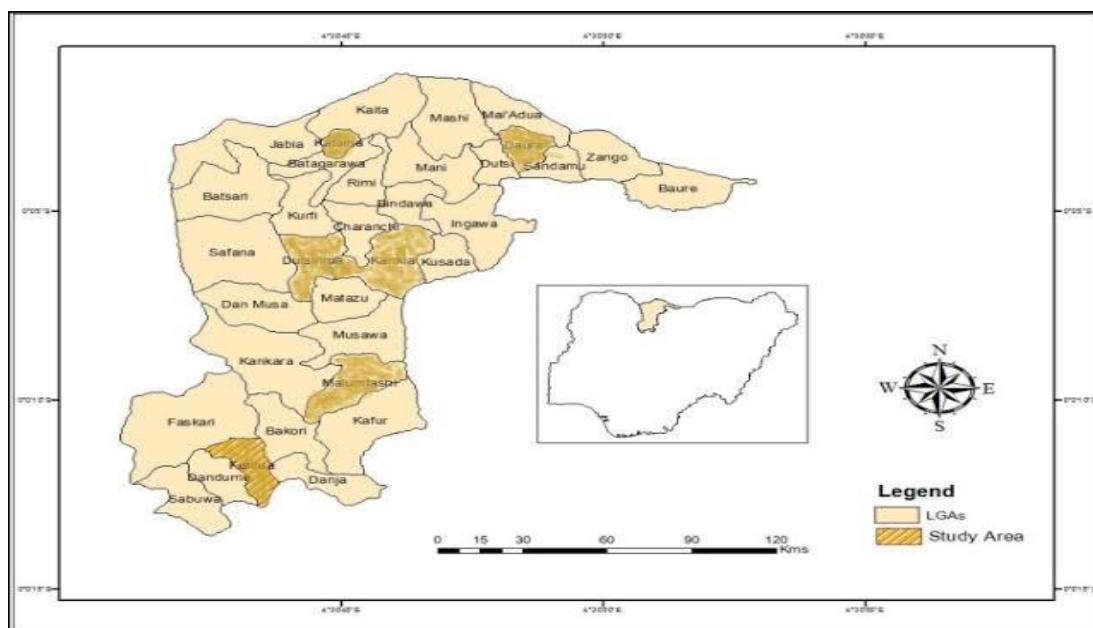


Figure 1: Katsina state map showing the study area (Source: Abaje *et al.*, 2016)

### 2.2 Sample collection and preparation

Samples were collected from each of the selected areas, labelled and stored in glass bottles with tight covers to prevent them from moisture and contamination after which they were stored in the refrigerator at 5°C until ready for use. The leaf samples were thoroughly washed with distilled water to dissociate sediment particles from it. The fresh leaves were cut into smaller pieces using dissecting kit, they were air dried for some minutes and later put in an oven at 55°C. The samples were then blended to powder using an electric blender. The resulting powder was put on a thermoplastic polypropylene sample holder and covered with cotton wool to prevent it from spraying. The samples were further encapsulated into irradiation capsules and heat sealed for neutron activation irradiation.

### 2.3 Quality control

For this investigation, the standard reference materials NIST 1515 (apple leaves) and NIST 1547 (peach leaves) were used concurrently as comparator reference standards and control. The obtained elemental concentration and their respective uncertainties for the SRMs and the internal quality control compared to their respective reference values was shown in tables 1 and 2. We calculated the U-score, Z-score, and relative bias (RB) in order to assess the lab performance. The following formulae were used to calculate these measurements:

$$U - score = \frac{|X_{Lab} - X_{Ref}|}{\sqrt{\mu_{Lab}^2 + \sigma_{Ref}^2}} \quad (1)$$

$$Z - score = \frac{|X_{Lab} - X_{Ref}|}{\mu_{Lab}} \quad (2)$$

$$R - bias = \frac{X_{Lab} - X_{Ref}}{X_{Ref}} \times 100 \quad (3)$$

Where;  $X_{LAB}$  represents the laboratory results,  $\mu_{LAB}$  is the standard deviation,  $X_{Ref}$  represents recommended uncertainty, and  $\sigma_{Ref}$  is the normal uncertainty.

The laboratory assessment is set as follows; satisfactory if U - score  $\leq 1$ , and satisfactory if Z - score is  $\leq 2$ , questionable for  $2 < Z - score < 3$ , and unsatisfactory if Z - score is  $\geq 3$ .

**Table 1: Comparison of obtained values with values in the certified reference materials (CRMs) of NIST 1515 (apple leaves).**

Elements (mg/kg)	NIST 1515 certified values	NIST 1515 recorded values	U-score	Z-score	R-bias
K	1.61 ± 0.02	1.43 ± 1.19	0.15	8.85	10.99
Al	286.00 ± 9.00	300.30 ± 17.30	0.73	1.59	5.00
Ba	49.00 ± 2.00	53.90 ± 7.30	0.65	2.45	9.60
Cl	579.00 ± 23.00	573.21 ± 23.90	0.18	0.25	-1.00
Mn	54.00 ± 3.00	57.24 ± 7.70	0.39	1.08	6.00
Br	1.80	1.49 ± 1.20	0.26	-	-17.20
La	20.00	27.60 ± 5.30	1.43	-	38.00
Sm	3.00	4.38 ± 2.09	0.66	-	46.00

Values represent mean ± standard deviation.

**Table 2: Comparison of obtained values with the certified values in the certified reference materials (CRMs) of NIST 1547 (peach leaves).**

Elements mg/kg	NIST 1547 Certified Values	NIST 1547 This work measured values	U-score	Z-score	R-bias
K	2.43 ± 0.03	2.65 ± 1.60	0.14	7.30	9.00
Al	249.00 ± 8.00	257.00 ± 16.03	0.45	1.00	3.21
Ba	124.00 ± 4.00	136.40 ± 11.80	1.00	3.10	10.00
Cl	360.00 ± 19.00	284.40 ± 16.90	2.97	3.90	-21.00
Mn	98.00 ± 3.00	104.86 ± 10.24	0.64	2.30	7.00
Br	11.00	10.45 ± 3.20	0.17	-	-5.00
La	9.00	9.36 ± 3.10	0.12	-	4.00
Sm	1.00	1.09 ± 1.04	0.09	-	9.00

Values represent mean ± standard deviation.

The illustrated values in tables (1 and 2) revealed that, the concentrations of the compared elements are in good agreement with the certified values of the two CRMs; NIST 1515 and NIST 1547. This calculation exposed a great

quality result found in this practice which could be achieved through the statistical assessment and evaluation. The statistical parameters U-score and Relative bias calculated for all elements are acceptable only Z-score shows no satisfaction in concentrations of some elements.

## 2.4 Irradiation and Measurements

Neutron activation analysis (NAA), and in particular instrumental neutron activation analysis (INAA), is a method with a very high degree of precision that is primarily used to determine the trace concentrations of elements in samples. This method is based on the measurement of the results of nuclear processes that transform stable nuclei into other, primarily radioactive nuclei.

For calculating the concentration of every element in the sample irradiated with reactor thermal neutron, we used the (IAEA, 1990) equation as follows:

$$\frac{w}{w_{st}} = \frac{N_s D_{st}}{N_{st} D} = \frac{N_s e^{-\lambda t d(st)}}{N_{st} e^{-\lambda t d}} \quad (4)$$

The concentration of the unknown element in the sample denoted by  $C_s$  is given by the following equation (IAEA, 1990).

$$C_s = \frac{W}{M} \quad (5)$$

The samples together with the standard reference materials (SRMs) NIST 1515 (Apple leaves) and NIST 1547 (Peach leaves) were irradiated using the Nigeria Research Reactor 1 (NIRR-1) under an average flux density of  $5.0 \times 10^{11} \text{ ncm}^{-2}\text{S}^{-2}$ . An irradiation time of 5 min was used for the determination of short-lived radionuclide elements and 6 hours for the determination of medium and long-lived radionuclides. A PC-based gamma-ray spectrometer set up was applied for the radioactivity measurement of induced radionuclides. It consists of High Purity Germanium detector (HPGe-coaxial type) coupled with a computer based multi-channel analyzer (MCA) through electronic modules.

## 2.5 Statistical Analysis

The statistical analysis procedure known as analysis of variance (ANOVA) divides the observed aggregate variability within a data set into systematic factors and random factors. The presented data set is statistically affected by the systematic factors but not by the random ones. In a regression analysis, analysts employ the ANOVA to ascertain the impact that independent variables have on the dependent variables. The analysis of variance gives simple correlation coefficient table showing the degree of dependence between two variables. In the simple correlation coefficient table, values outside the range of -1 to 1 indicate that something is wrong with the data and should be further analyzed or corrected.

## 2.6 Assessment of Daily Intake of Metals

The daily intake of the identified metals was evaluated using the equation below:

$$DIM = \frac{C_{metal} \times C_{factor} \times D_{intake}}{B_{weight}} \quad (6)$$

Where  $C_{metals}$ ,  $C_{factor}$ ,  $D_{intake}$ , and  $B_{weight}$  stand for heavy metal concentrations in the baobab leaf samples, conversion factor, daily intake of the samples, and the average body weight respectively. To convert the samples to dry weights, Jan et al. (2010) employed a conversion factor (CF) of 0.085. The average body weight for the adult and pediatric populations was 60 kg (Orisakwe *et al.*, 2015) and 24 kg (Ekhatior *et al.*, 2017) respectively; these values were also used for the calculation of HRI. The average daily intake of the samples was  $0.527 \text{ kg person}^{-1} \text{ d}^{-1}$  (Balkhaira *et al.*, 2015).

2.7 Health Risk Assessment (THQ)

Non-carcinogenic risks for individual heavy metal for vegetable were evaluated by computing the target hazard quotient (THQ) using the following equation (Micheal *et al.*, 2015).

$$THQ = CDI/R_fD \tag{7}$$

CDI is the chronic daily heavy metal intake (mg/kg/day) presented in tables 5 and 6, and R<sub>f</sub>D is the oral reference dose (mg/kg/day) which is an estimation of the maximum permissible risk on human population through daily exposure. The following reference doses were used (Cu = 30, As = 1, Fe = 0.7, Mn = 0.18, Cr = 0.3, Zn = 40, Br = 1, U = Co = 0.13, V = 0.5). To evaluate the potential risk to human health through more than one heavy metal, chronic hazard index (HI) is obtained as the sum of all hazard quotients (THQ) calculated for individual heavy metals for a particular exposure pathway [NFPCSP, 2011]. It is calculated as follows:

$$HI = THQ_1 + THQ_2 + \dots + THQ_n \tag{8}$$

Where 1, 2, ..., n are the individual heavy metals or vegetables and fruit species. It is assumed that the magnitude of the effect is proportional to the sum of the multiple metal exposures. The calculated HI is compared to standard levels in which the population is assumed to be safe when HI < 1 and in a level of concern when 1 < HI < 5 (Guerra *et al.*, 2012).

3. RESULTS AND DISCUSSION

3.1 Concentrations of the Identified Elements in the Analyzed Baobab Samples

Six (6) samples from six (6) different locations in Katsina State were obtained and analyzed using Instrumental Neutron Activation Analysis (INAA). The outcome of the analysis displayed twenty-two (22) chemical elements from the analyzed samples which includes; Mg, Al, Cl, Ca, V, Cu, Mn, Fe, Co, Zn, Cr, Na, K, As, Br, Sr, La, Sm, U, Sc, Rb, and Th, as shown in table 3 below.

Table 3: Concentrations (mg/kg) of the identified elements in the baobab leaf samples from different locations of Katsina State.

Element s	DAURA	DUTSINMA	FUNTUA	KANKIA	KATSINA	MALUMFASHI
Mg	2688 ± 89	3233 ± 87	3147 ± 85	3851 ± 116	3067 ± 83	4321 ± 173
Al	752 ± 14	888 ± 13	418 ± 9	325 ± 20	772 ± 12	1852 ± 239
Cl	2096 ± 36	3220 ± 42	52161 ± 52	2972 ± 42	3019 ± 42	3944 ± 55
Ca	12550 ± 502	19120 ± 612	20680 ± 641	27910 ± 893	24870 ± 672	34610 ± 1454
V	1.81 ± 0.300	1.58 ± 0.180	2.84 ± 0.280	BDL	2.75 ± 0.26	10.8 ± 2.6
Cu	BDL	1.410	BDL	2.42	BDL	BDL
Mn	442 ± 100	53.9 ± 0.300	116 ± 1	54.5 ± 0.3	65.7 ± 0.3	108 ± 0.4
Sr	17.70 ± 4.80	50.300	67.10 ± 4.60	89.2 ± 3.7	67.1 ± 3.8	103 ± 5
Na	128 ± 1	202 ± 1	1970 ± 4	290 ± 1	345 ± 1	121 ± 1
K	12110 ± 97	12070 ± 97	14970 ± 104	7484 ± 67	15310 ± 107	10280 ± 93
As	0.086	0.30 ± 0.050	BDL	BDL	BDL	0.11 ± 0.03
Br	31.7 ± 0.200	37.5 ± 0.200	18.90 ± 0.1	27.8 ± 0.1	16.0 ± 0.1	19.1 ± 0.1
La	15.5 ± 0.900	4.72 ± 0.060	6.97 ± 0.08	4.29 ± 0.05	1.63 ± 0.04	3.64 ± 0.05
Sm	1.46 ± 0.010	0.40 ± 0.010	0.45 ± 0.01	0.293 ± 0.004	0.188 ± 0.004	0.325 ± 0.04

U	0.068 ± 0.011	0.021	BDL	BDL	BDL	BDL
Sc	0.18 ± 0.010	0.17 ± 0.010	0.11 ± 0.01	0.08 ± 0.01	0.19 ± 0.01	0.19 ± 0.01
Cr	2.45 ± 0.410	1.90 ± 0.400	1.47 ± 0.39	1.24 ± 0.32	0.94	0.51
Fe	900 ± 88	877 ± 72	1670 ± 95	506 ± 66	1070 ± 75	1190 ± 0.75
Co	3.49 ± 0.120	0.60 ± 0.070	0.32 ± 0.09	0.41 ± 0.05	0.28 ± 0.04	0.31 ± 0.06
Zn	24.5 ± 4.100	13.3 ± 3.200	18.3 ± 0.5	9.05	4.93	12.0 ± 0.3
Rb	3.860	6.01 ± 1.680	9.21 ± 1.28	5.31 ± 0.95	5.37 ± 0.15	6.75 ± 1.19
Th	0.54 ± 0.070	0.43 ± 0.060	0.33 ± 0.05	0.25 ± 0.04	0.33 ± 0.05	0.66 ± 0.07

These elements are of significant concentrations in the various samples obtained from different locations of Katsina state. From the result obtained, the following can be deduced; Magnesium (Mg) contents in the analyzed samples ranged between (2688 ± 89 – 4321 ± 173 mg/kg). The highest concentration of Mg was observed in Malumfashi baobab leaves while the lowest was in Daura baobab leaves. Magnesium is required for energy production, oxidative phosphorylation, and glycolysis (Rude *et al.*, 2012). Magnesium is an essential element in biological systems of humans. It is a cofactor in more than 300 enzyme systems that regulate diverse biochemical reactions in the body including protein synthesis, muscle and nerve function, blood glucose control, and blood pressure regulation. An adult body contains approximately 25 g of magnesium, with 50% to 60% present in the bone and most of the rest in soft tissues (Volpe *et al.*, 2012). The maximum guideline of Mg intake established by FNB is 350 mg (FNB, 1997).

Aluminum (Al) concentrations were between the range of (325 ± 20 – 1852 ± 239 mg/kg) in the analyzed samples. The highest value of Al was recorded in Malumfashi baobab leaves while the lowest was found in Kankia baobab leaves. High level of Al in baobab may be attributed to regular mining and processing of aluminium ores or production of aluminium metal, alloys, and compounds in the area (ATSDR, 2008). Aluminium forms about 8% of the earth's crust and is the third most abundant element after oxygen and silicon (Gupta *et al.*, 2013; Herndon, 2015). Exposure to aluminium at high level through food and to a lesser extent, the environment along with occupational exposure may have deleterious effects on human health. The main route for transfer of aluminium into the human body is by inhalation (Riihimaki and Aitio, 2012; Whillhite *et al.*, 2014). According to WHO, the acceptable daily intake of aluminium is 1 mg/kg of body mass (Alasfar and Isaifan, 2021).

Chlorine (Cl) is one of the identified elements in the studied biological samples. It concentrations ranged (2096 ± 36 – 52161 ± 52 mg/kg), with the highest concentration detected in Funtua baobab leaves and the lowest in Daura baobab leaves. Chlorine is essential to life, it is mostly present in cell fluid as a negative ion to balance the positive ions (Emsley, 2011). The upper tolerable intake of chlorine set by IOM is 51.1 mg/kg. This indicates that, Cl concentrations in all the analyzed samples exceeded the maximum guideline.

The concentration of Calcium (Ca) in all the studied samples range from (12550 ± 502 – 34610 ± 1454 mg/kg). The sample with highest level was noticed in Malumfashi baobab leaves while the lowest in Daura baobab leaves. Previous studies also reported high level of calcium in *A. digitata* leaves (Smith *et al.*, 1996; Glew *et al.*, 1997). Baobab leaves are very rich in calcium according to literature (Chadare *et al.*, 2009). Calcium makes up much of the structure of bones and teeth and allows normal bodily movement by keeping tissue rigid, strong, and flexible (IOM, 2011). Almost all 98% calcium in the body is stored in the bones, and the body uses the bones as a reservoir for and source of calcium to maintain calcium homeostasis (IOM, 2011). The upper tolerable intake of calcium is 35.7 mg/kg (IOM, 2011). Other authors (Yazzie *et al.*, 1994; Sena *et al.*, 1998; Boukari *et al.*, 2001) reported calcium concentrations lower than the detected concentrations in the present study.

Vanadium (V) is one of the identified elements in the present study. Its concentrations ranged between (1.58 ± 0.18 – 10.8 ± 2.6 mg/kg) in all the analyzed samples. The highest concentration was observed in Malumfashi baobab leaves while the lowest in Dutsin-ma baobab leaves. Vanadium is a trace element essential to roots and stems of plants. Foods that contain relatively high amount of vanadium are mushrooms, parsley, spinach, and oysters (Encyclopedia, 2019). Vanadium enters the food chain through the plants in the soil. Dietary intake of vanadium in general population was reported at 6-18 µg/day (Pennington and Jones, 1987). High concentration of vanadium in

Malumfashi baobab leaves may be attributed to anthropogenic activities in the area such as mining, fossil fuel and coal combustion, use of fertilizers and pesticides.

Copper (Cu) contents were only detected in Dutsin-Ma and Kankia baobab leaves with 1.41 and 2.42 mg/kg concentrations respectively. Other samples from the remaining locations were at BDL. Copper is an essential trace mineral necessary for survival. It is found in all body tissues and plays a vital role in making red blood cells and maintaining nerve cells and the immune system (Debra, 2017). Deficiency of copper can lead to cardiovascular diseases and other problems. The maximum intake limit for adults aged 19 years and above is 10 mg/day (DHHS, 2015). An intake above this level could be toxic. Similar studies reported Cu concentrations in baobab leaves of 0.29 mg/100 gdw (Smith *et al.*, 1996) and 1.6 mg/100 gdw (Glew *et al.*, 1997).

Manganese (Mn) concentrations in the studied samples ranged between ( $53.9 \pm 0.3 - 442 \pm 1$  mg/kg). The highest level was recorded in Daura baobab leaves while the lowest in Dutsin-ma baobab leaves. Previous study also reported manganese concentrations in baobab leaves (Yazzie *et al.*, 1994). Mn is an essential element in virtually all living organisms (Andresen *et al.*, 2018). In excess amount, manganese can cause toxicity. Manganese toxicity mainly affects the central nervous system and can cause tremors, muscle spasms, tinnitus, and hearing loss (Nielsen, 2012; Butchman, 2014). The upper tolerable intake limit of Mn is 0.16 mg/kg (NIH, 2021). This shows that, Mn concentrations in all the analyzed samples exceeded the established guideline.

Sodium (Na) content in the analyzed samples ranged between ( $121 \pm 1 - 1970 \pm 4$  mg/kg). The highest concentration was detected in Funtua baobab leaves and the lowest in Malumfashi baobab leaves. Sodium is an essential nutrient required for maintenance of plasma volume, acid base balance, transmission of nerve impulses and normal cell function (Widmaier, 2008). According to Ibrahim and Emmanuel (2023), the maximum guideline of sodium intake is 32.9 mg/kg. Therefore, sodium concentrations in all the studied samples exceeded the maximum guideline.

Potassium (K) shows significant concentrations in all the analyzed samples. Its concentration levels ranged between ( $7484 \pm 67 - 15310 \pm 107$  mg/kg), with Katsina Baobab leaves recording the highest concentration and Kankia baobab leaves recorded the lowest. Other study also reported potassium content in baobab (Yazzie *et al.*, 1994). Potassium is an essential nutrient that is naturally present in many foods and available as a dietary supplement (IOM, 2005). The upper allowable intake of potassium is 50.1 mg/kg (WHO, 2012). Thus, potassium contents in all the studied samples exceeded the WHO established guideline.

Chromium (Cr) plays a role in carbohydrate, lipid, and protein metabolism by potentiating insulin action (Coates *et al.*, 2010; EFSA, 2014). Chromium is considered to be an essential nutrient based on its insulin action (FNB, 2001). In the present study, chromium concentrations are of the range ( $0.51 - 2.45 \pm 0.41$  mg/kg). The highest level was detected in Daura baobab leaves while the lowest in Malumfashi baobab leaves. Previous researches also recorded chromium concentrations in baobab leaves (Mohammed *et al.*, 2016; Yaradua *et al.*, 2019; Rabiou *et al.*, 2021). According to EFSA (2014), the maximum guideline for Cr intake is 0.3 mg/kg. Thus, Cr concentrations in all the studied samples are above the EFSA's permissible limit.

Iron (Fe) shows concentration within the range of ( $506 \pm 66 - 1670 \pm 95$  mg/kg). The highest concentration was measured in Funtua baobab leaves while the lowest in Kankia baobab leaves. Other studies (Yazzie *et al.*, 1994; Smith *et al.*, 1996; Yaradua *et al.*, 2019; Rabiou *et al.*, 2021) also measured Fe concentrations in baobab leaves lower than the concentrations measured in the present study. Iron is an essential component of hemoglobin, an erythrocyte (red blood cell) protein that transfers oxygen from the lungs to the tissue (Wessling *et al.*, 2014). The maximum permissible limit for adult is 0.64 mg/kg (FNB, 2001). This shows that, Fe concentrations in all the analyzed samples exceeded the maximum permissible limit.

Zinc (Zn) concentration in the analyzed samples ranged between ( $4.93 - 24.5 \pm 4.1$  mg/kg). The highest content was recorded in Daura baobab leaves while the lowest in Katsina baobab leaves. Some Studies also reported Zinc contents in baobab leaves (Yazzie *et al.*, 1994; Smith *et al.*, 1996; Yaradua *et al.*, 2019; Rabiou *et al.*, 2021). According to WHO/FAO (1989), the maximum guideline for Zn intake is 40 mg/kg. This clearly shows that, Zn



concentrations in all the analyzed samples are lower than the established guidelines. Zinc is an essential nutrient found in a variety of plant and animal foods, along with supplements (Jillian, 2022). It plays a key role in skin health, immune function, and cell growth and may protect against acne, inflammation, and other conditions (Jillian, 2022). Cobalt (Co) shows concentrations of the range ( $0.28 \pm 0.04 - 3.49 \pm 0.12$  mg/kg). The highest concentration was noticed in Daura baobab leaves while the lowest in Katsina baobab leaves. Cobalt is an important component in human nutrition as it is an essential part of vitamin B<sub>12</sub> (NCBI, 2023). A safe recommended dietary allowance for cobalt has not been set yet (NCBI, 2023). Adverse effects related to cobalt toxicity can occur at levels of 7 to 10 µg/L or more (Venkatraman, 2020).

Arsenic (As) was only detected in Daura, Dutsin-ma, and Malumfashi baobab leaf samples. Other samples from the remaining study areas were at BDL. The range of As concentration in Daura, Dutsin-ma, and Malumfashi are between the range ( $0.086 - 0.30 \pm 0.5$  mg/kg), where Dutsin-ma baobab leaves recorded the highest content while Daura baobab leaves shows the lowest. Arsenic is highly toxic in its inorganic form (WHO, 2022). Long term exposure to arsenic from drinking water and food can cause cancer and skin lesions and it has also been associated with cardiovascular disease and diabetes (WHO, 2022). The maximum As intake guideline established by the Malaysian Food and Regulation is 1 mg/kg (MFR, 1985). This indicates that, the detected As concentrations in the three study areas are well below the MFR guidelines.

Bromine (Br) concentrations ranged between ( $16.0 \pm 0.1 - 37.5 \pm 0.2$  mg/kg). The highest level was observed in Dutsin-ma baobab leaves while the lowest was in Katsina baobab leaves. Bromine is corrosive to human tissue in a liquid state and its vapors irritate eyes and throat (Lenntech, 2023). Human can absorb organic bromines through the skin with food and during breathing (Lenntech, 2023). In its organic form, it can cause damage to organs such as liver, kidneys, lungs, and they can cause stomach and gastrointestinal malfunctioning (Lenntech, 2023). In 1989, JMPR established the maximum daily intake limit of 1.0 mg/kg for bromine. Hence, Br concentrations in all the analyzed samples exceeded the JMPR maximum guideline.

Uranium (U) was only detected in Daura and Dutsin-ma baobab leaves, with Daura recording the highest level. Uranium concentration in baobab leaves of the remaining location are at BDL. The detected U concentrations in Daura and Dutsin-ma baobab leaves are  $0.068 \pm 0.011$  and  $0.021$  mg/kg respectively. Uranium is a heavy metal that can enter the body through the mouth, nose and skin, threatening human health (Wang *et al.*, 2020). Its exposure to human is mainly derived from the soil-crop system as it is easily integrated into the food chain (Li *et al.*, 2019a). It is highly hazardous to human health via affecting metabolic activity (Malaviya and Singh, 2012; Liang *et al.*, 2020). Human daily intake of uranium has been estimated to range from 0.9 to 1.5 mg/day (ATSDR, 2015). This range is equivalent to 0.01 to 0.02 mg/kg body weight. Thus, Uranium concentrations in Daura baobab leaves is above the ATSDR limit while its concentration in Dutsin-ma baobab leaves is within the estimated limit.

In the present study, some of the identified elements are known to be non-essential to human. Elements such as Sm, La, Sc, Rb, Sr, and Th, are considered to be non-essential and does not have any biological role in the human body. According to researches, Rubidium, Samarium, Scandium, and Lanthanum have no known biological role (Thomas, 2014; Emsley, 2015; Crans and Kostenkova, 2020). Their concentrations in the analyzed samples are Rb ( $3.86 - 9.21 \pm 1.28$  mg/kg), Sm ( $0.188 \pm 0.004 - 1.46 \pm 0.01$  mg/kg), Sc ( $0.08 \pm 0.01 - 0.19 \pm 0.01$  mg/kg), La ( $1.63 \pm 0.04 - 15.5 \pm 0.9$  mg/kg), Sr ( $17.7 \pm 4.8 - 103 \pm 5$  mg/kg), and Th ( $0.25 \pm 0.04 - 0.66 \pm 0.07$  mg/kg). These elements do not play any significant role in meeting nutritional demands. They do not have any known function in the human body (Rawn *et al.*, 2011; AESAN, 2015).

### 3.2 Statistical Analysis

The detected concentrations from the analyzed biological samples were further subjected to statistical analysis using the Analysis of Variance (ANOVA). The ANOVA test was employed to evaluate the impact that the independent variables have on the dependent variables in a regression study. The result of this analysis presents statistically significant differences in mean concentrations of (Mg, Ca), (Al, V), (Al, Th), (Cl, Rb), (Ca, Sr), (Ca, Cr), (Sr, U), (Sr, Cr), (Sr, Co), (Na, Rb). The P - value was set at  $P < 0.01$  and  $P < 0.05$ . The inter-elemental correlations between the mean concentrations of the identified elements were presented in Table 4 below.

Table 4: Inter elemental correlations between mean concentrations of the studied baobab samples

	Mg	Al	Cl	Ca	V	Cu	Mn	Sr	Na	K	As	Br	La	Sm	U	Sc	Cr	Fe	Co	Zn	Rb	Th	
Mg	1																						
Al	0.547	1																					
Cl	-0.172	-0.356	1																				
Ca	0.927**	0.520	-0.142	1																			
V	0.624	0.921**	-0.037	0.639	1																		
Cu	0.297	-0.409	-0.300	0.134	-0.524	1																	
Mn	-0.533	-0.009	-0.100	-0.644	-0.072	-0.420	1																
Sr	0.910*	0.349	0.047	0.970**	0.523	0.225	-0.733	1															
Na	-0.210	-0.441	0.992**	-0.149	-0.122	-0.257	-0.148	0.048	1														
K	-0.638	-0.112	0.484	-0.395	-0.026	-0.719	0.068	-0.381	0.509	1													
As	-0.007	0.379	-0.340	-0.208	0.082	0.175	-0.038	-0.266	-0.397	-0.103	1												
Br	-0.257	-0.182	-0.372	-0.543	-0.476	0.538	0.268	-0.541	-0.396	-0.391	0.722	1											
La	-0.569	-0.188	0.062	-0.751	-0.236	-0.252	0.950**	-0.775	0.011	0.016	0.039	0.432	1										
Sm	-0.576	-0.091	-0.095	-0.736	-0.189	-0.293	0.981**	-0.802	-0.144	0.022	0.086	0.437	0.982**	1									
U	-0.623	-0.060	-0.288	-0.783	-0.263	-0.191	0.910*	-0.876*	-0.328	0.014	0.299	0.604	0.906*	0.956**	1								
Sc	-0.161	0.700	-0.451	-0.061	0.502	-0.634	0.285	-0.271	-0.491	0.386	0.414	-0.050	0.060	0.213	0.338	1							
Cr	-0.774	-0.470	0.012	-0.951**	-0.634	0.069	0.672	-0.924**	0.002	0.107	0.330	0.742	0.813*	0.792	0.849*	-0.028	1						
Fe	-0.127	0.155	0.809	-0.012	0.415	-0.747	-0.016	0.055	0.771	0.720	-0.186	-0.574	-0.008	-0.081	-0.236	0.132	-0.184	1					
Co	-0.584	-0.087	-0.247	-0.719	-0.228	-0.244	0.970**	-0.812*	-0.284	-0.015	0.090	0.458	0.940**	0.984**	0.974**	0.271	0.777	-0.212	1				
Zn	-0.464	-0.087	0.311	-0.685	-0.077	-0.327	0.825*	-0.666	0.234	0.096	0.156	0.392	0.930**	0.873*	0.769	0.024	0.743	0.255	0.775	1			
Rb	0.244	-0.001	0.864*	0.274	0.289	-0.211	-0.474	0.436	0.840*	0.340	-0.133	-0.450	-0.342	-0.476	-0.619	-0.334	-0.368	0.796	-0.620	-0.014	1		
Th	0.243	0.875*	-0.291	0.119	0.772	-0.516	0.444	-0.053	-0.401	-0.088	0.425	0.060	0.308	0.388	0.385	0.705	-0.039	0.165	0.367	0.387	-0.140	1	

Inter-elemental correlations of.....

- \*\* . Correlation is significant at the 0.01 level (2-tailed).
- \* . Correlation is significant at the 0.05 level (2-tailed).

Significant positive correlations were observed between Ca – Sr ( $r = 0.970$ ,  $P < 0.05$ ). Also, a significant negative correlation was noticed between Ca – Cr ( $r = -0.951$ ,  $P < 0.05$ ). Moreover, high positive correlations were detected between some elements, e.g. Mg – Ca, Mg – Sr, Al – V, Al – Th, Cl – Rb, Na – Rb, with the values 0.927, 0.910, 0.921, 0.875, 0.864, and 0.840 respectively. More so, strong negative correlations were detected between some element pairs, e.g. Sr – Cr, Sr – U, and Sr –Co with the values -0.924, -0.876, and -0.812 respectively. In this data, no positive or inverse perfect correlation was detected between any of the element pairs. This indicates that, there is no positive or negative perfect relationship between the concentrations of the elements in these studied samples.

### 3.3 Estimated Daily Intake of Heavy Metals

Tables 5 and 6 show the estimated daily intake (EDI) of the heavy metals detected from the analyzed samples. In the present study, the estimated daily intake of the heavy metals (As, Br, U, Cr, Co, Mn, Fe, Zn, Cu, and V) in both adults and children are less than the suggested daily intake limit established by USEPA.

**Table 5: Daily intake of essential and toxic heavy elements in adults through baobab leaves consumed in Katsina state.**

Locations	Essential Elements							Toxic Elements		
	Cu	Zn	Fe	Mn	Co	Cr	V	As	Br	U
Daura	BDL	0.0183	0.6719	0.3299	0.0026	0.0018	0.0014	0.0001	0.0237	0.0001
Dutsin-Ma 1	0.001	0.0099	0.6548	0.0402	0.0005	0.0014	0.0012	0.0002	0.0279	0.0002
Funtua	BDL	0.0137	1.2468	0.0866	0.0002	0.0011	0.0021	BDL	0.0141	BDL
Kankia 8	0.001	0.0068	0.3778	0.0407	0.0003	0.0009	BDL	BDL	0.0208	BDL
Katsina	BDL	0.0037	0.7988	0.0491	0.0125	0.0007	0.0021	BDL	0.0119	BDL
Malumfashi	BDL	0.0089	0.8884	0.0806	0.0002	0.0004	0.0081	0.0001	0.0143	BDL

**Table 6: Daily intake of essential and toxic heavy elements in children through baobab leaves consumed in Katsina state.**

Locations	Essential Elements							Toxic Elements		
	Cu	Zn	Fe	Mn	Co	Cr	V	As	Br	U
Daura	BDL	0.0457	1.6798	0.8249	0.0065	0.0046	0.0034	0.0002	0.0592	0.0001
Dutsin-Ma	0.0026	0.0248	1.6369	0.1006	0.0011	0.0035	0.0029	0.0006	0.0699	0.00004
Funtua	BDL	0.0342	3.1169	0.2165	0.0006	0.0027	0.0053	BDL	0.0353	BDL
Kankia	0.0045	0.0169	0.9444	0.1017	0.0007	0.0023	BDL	BDL	0.0519	BDL
Katsina	BDL	0.0092	1.9971	0.1226	0.0314	0.0018	0.0051	BDL	0.0299	BDL
Malumfashi	BDL	0.0224	2.2211	0.2016	0.0006	0.0009	0.0202	0.0002	0.0356	BDL

### 3.4 Health Risk Target Hazard Quotient

The (THQ) for non-cancer risk of the detected heavy metals through the consumption of the baobab leaves for both adults and children living in the study areas are determined and displayed in tables 7 and 8.

**Table 7: Heavy metal target hazard quotient and health risk index in adults from consuming harvested baobab leaves from Katsina state.**

Locations	Essential Elements							Toxic Elements			HRIs
	Cu	Zn	Fe	Mn	Co	Cr	V	As	Br	U	
Daura	BDL	0.000	0.8399	2.0619	0.0200	0.0060	0.0028	0.0001	0.0237	0.0040	2.9589
Dutsin-Ma 1	0.000	0.000	0.8185	0.2513	0.0038	0.0047	0.0024	0.0002	0.0279	0.0080	1.1171
Funtua 3	BDL	0.000	1.5585	0.5413	0.0015	0.0037	0.0042	BDL	0.0141	BDL	2.1236

Kankia	0.000 1	0.000 2	0.4723	0.2544	0.0023	0.0030	BDL	BDL	0.0208	BDL	0.7531
Katsina	BDL	0.000 1	0.9985	0.3069	0.0961	0.0023	0.0042	BDL	0.0119	BDL	1.4200
Malumfashi	BDL	0.000 2	1.1105	0.5038	0.0015	0.0013	0.0162	0.0001	0.0143	BDL	1.6479

**Table 8: Heavy metal target hazard quotient and health risk index in children from consuming harvested baobab leaves from Katsina state.**

Locations	Essential Elements							Toxic Elements			HRIs
	Cu	Zn	Fe	Mn	Co	Cr	V	As	Br	U	
Daura	BDL	0.0011	2.0998	5.1556	0.0500	0.0153	0.0068	0.0012	0.0592	0.0040	7.3920
Dutsin-Ma	0.0008	0.0006	2.0461	0.6288	0.0085	0.0117	0.0058	0.0006	0.0699	0.0016	2.7444
Funtua	BDL	0.0009	3.8961	1.3531	0.0046	0.0090	0.0106	BDL	0.0353	BDL	5.3096
Kankia	0.0002	0.0004	1.1805	0.6356	0.0054	0.0077	BDL	BDL	0.0519	BDL	1.8817
Katsina	BDL	0.0002	2.4963	0.7663	0.2415	0.0060	0.0102	BDL	0.0299	BDL	3.5504
Malumfashi	BDL	0.0006	2.7764	1.2600	0.0046	0.0030	0.0404	0.0006	0.0356	BDL	4.1206

The THQ has been recognized as a useful parameter for evaluating the risk associated with the consumption of metals contaminated foods. THQ is interpreted as either greater than 1 ( $> 1$ ) or less than 1 ( $< 1$ ), where  $THQ > 1$  shows human health risk concern (Bassey *et al.*, 2014). The risk level ( $THQ < 1$ ) was observed for all the identified heavy metals for both adult and children except for Fe and Mn which showed risk levels ( $THQ > 1$ ) in some locations. This indicates that, the accumulation of these metals through baobab leaves consumption does not have any considerable health risk except for Fe and Mn which may pose a non-cancer risk to inhabitants through the consumption of baobab leaves in some of the locations. For all the samples, THQ is in the order  $Mn > Br > Co > Cr > V > Zn > U > As > Cu$ . This order was the same for both adults and children despite that the children have higher THQ values in all cases. This corroborates the findings of (Mahfuza *et al.*, 2017; Yaradua *et al.*, 2019). Accordingly, the non-cancer risks for each sample were expressed as the cumulative HI, which is the sum of individual THQ. The risk level ( $HI > 1$ ) was observed for all the studied samples except for Kankia which shows adult risk level ( $HI < 1$ ). Moreover, the highest risk level (HI) was observed in the samples from Daura and lowest in the samples from Kankia. Hence, it is deduced that the inhabitants of Katsina state may be exposed to non-carcinogenic health risk through the consumption of heavy metals via baobab leaves and therefore it is recommended that crucial measures should be employed to reduce the level of heavy metals contamination in baobab leaves of Katsina state to protect its inhabitants from the non-carcinogenic health risk resulting from the consumption of baobab leaves.

**CONCLUSION**

The present study determined and assessed the heavy metals concentrations in baobab leaves from Katsina state, Nigeria using NAA method. Also, a statistical analysis was performed using Analysis of variance (ANOVA). From the findings, it is deduced that the mean concentrations of all the identified heavy metals are higher than the USEPA, WHO/FAO and maximum tolerable limits except for As, Zn and Cu which showed concentrations lower than the established guidelines. Accordingly, the result for the statistical analysis revealed a significant positive and negative correlation between some element pairs, a high negative and positive correlation between some elements, while no perfect positive or negative correlation was detected between any of the element pairs. The results also depicted that, with the exception of Mn, and Fe in Daura, Funtua/Malumfashi, and Fe for children in all the studied locations, the estimated daily intake of the detected heavy metals was lower than the recommended daily intake limit stated by USEPA (2002). Moreover, the Target Hazard Quotient ( $THQ > 1$ ) was observed for all the identified heavy metals in all the studied locations except for Kankia which showed ( $THQ < 1$ ) for adult

population. Therefore, it is deducted that the consumption of baobab leaves from Katsina is of public health concern as it may increase the population cancer risks.

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