Levels of Heavy Metals in Soya Bean and Some Cereal Samples from Shani and Kwayakusar Local Government Areas in Borno State, Nigeria

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Authors' contributions

This work was carried out in collaboration among all authors. Author IBL designed the study, carried out part of the sampling, wrote the protocol and wrote the first draft of the manuscript. Author MCZ also carried out part of the sampling and helped in editing the manuscript. Author IMA also carried out part of the sampling and helped in literature review. Author MZ was also involved in sampling and helped in writing the protocol. Author CAJ managed the statistics and analyses of the study. All authors read and approved the final manuscript.

ABSTRACT

Grain (soya beans, sorghum and maize) samples from Shani and Kwayakusar Local Government Areas, Borno State, Nigeria were collected in agricultural locations for the determination of heavy metals. The levels of heavy metals were determined using Atomic Absorption Spectroscopy (AA–6800 SHIMADZU). The levels of all the heavy metals studied in all the agricultural locations were higher in the post-harvest grains than in the pre-harvest grains. Results from the Incremental Lifetime Cancer Risk (ILCR) showed that, there was the possibility of developing cancer related diseases from the consumption of cereal samples from the study area with respect to the $10^{-4}$ tolerable limit. The results further suggested that the source of these heavy metals content in the

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grains samples might be largely as a result of the application of agrochemicals. Hence, consumption of the study cereals from the study area is of health risk with respect to Pb, Cd and As and should be given higher priority by relevant agencies.

**Keywords:** Heavy metals; cereals; daily intake; average daily dose.

### 1. INTRODUCTION

The study of contamination of soil by heavy metals have gained much interest due to their influence on ground and surface water [1,2] and also on flora [3,4], animals and humans [5]. The behaviour of metals chemically through sorption and desorption are mostly governed by metal cation release from various sources like the application of agrochemicals, smelter dust, cation exchange, which are generally controlled by soil composition and pH, as cited by [6].

Toxic heavy metals ingestion by human and animals is mostly through uptake by plants which eventually gets into the food chain. Accumulation of these non-degradable heavy metals pose a great threat to human health and therefore should be checked. Metals mobility and bioavailability to living organisms are due to their chemical reactivity in the environment; hence they are easily exposed to people through breathing, drinking water or ingestion of food [7].

As a result of human activities the concentration of heavy metals increases and their study is of interest as reported by [8]. [9] reported studies have shown that concentration of heavy metals are lesser in crops cultivated on non-contaminated soil when compared to the ones cultivated on contaminated soil. In study carried out by [10], reported that anthropogenic sources such as waste incineration, vehicle exhaust and others cause accumulation of metal and metalloids in our agricultural soil, as a result of soil to plant transfer of metals, this causes food safety issues and potential health risk. [11] also reported that accumulation of toxic elements, especially through food ingestion is estimated through soil to plant transfer factor. Relationship between metal concentration in soil and long term irrigation revealed increase in total heavy metals in study carried out by [12].

The need to improve agricultural yields has resulted in the intentional addition of substances such as pesticides, fertilizers and other amendments to soils. Hence the need to access the level of some heavy metals in soil and grain samples from the area.

### 2. MATERIALS AND METHODS

#### 2.1 Study Area

Shani and Kwayakusar Local Government areas are located in Biu province (10.611°N and 12.195°E), which has favourable weather condition for the most part of the year though relatively cold from December to February. The rainy season lasts for about five months (June – October) with an average rainfall of about 700 – 1000 mm per annum [13]. It is characterized by physical features that are predominantly plateaus. There are also creeks and streams. The area is a characteristic Guinea savannah vegetative zone with grass cover, bushes and orchards. The areas along the creeks’ and hill sides are green all year round. The climate is favourable for cultivation of arable crops. People in the area are predominantly farmers.

#### 2.2 Sample Collection

Grain samples (soya beans, sorghum and maize) were collected from Shani and Kwayakusar Local Government agricultural locations. The grains to be planted were collected from the farmers before plantation which signify the pre-harvest and the harvested grains from the respective farms signify post-harvest. Soya beans, maize and sorghum were collected in a clean polythene bags which included pre and post-harvest. All samples were labelled appropriately, stored in cool container and transported to the Chemistry Department Research Laboratory, University of Maiduguri for further analysis. Grain samples from the agricultural locations were collected three times a month for a period of two years.

#### 2.3 Samples Preparation

Digestion of the Grain Samples for Heavy Metals Analysis.

Grains were ground and after which 1.00 g sample was digested for 3 h at 85°C with a conc. HNO₃: HCl (3:1) mixture. Then, conc. HClO₄ (1 mL) was added. The solution was filtered and diluted to 50 mL with distilled water [14]. Analysis was carried out using Atomic Absorption Spectrophotometer (AAS) with model number A–6800 SHIMADZU.
2.4 Average Daily Dose (ADD: mg kg\(^{-1}\) day)

Average daily dose upon the consumption of cereals was carried out using the equation below:

\[
\text{Average Daily Dose} = \frac{C \times \text{IR} \times \text{EF} \times \text{ED}}{\text{BW} \times \text{AT}} \tag{15}
\]

Where, \(C\) = Contaminant concentration in cereals (mg kg\(^{-1}\)); \(\text{IR}\) = Ingestion rate per unit time or event (kg day\(^{-1}\)); \(\text{EF}\) = Exposure frequency (days/year); \(\text{ED}\) = Exposure duration (70 years; lifetime; by convention) is the length of time that a receptor is exposed via a specific exposure pathway; \(\text{BW}\) = Body weight; \(\text{AT}\) = Pathway specific period of exposure for non-carcinogenic effects (i.e., \(\text{ED} \times 365\) days/year), and 70 year lifetime for carcinogenic effects (70 years \(\times 365\) days/year).

2.5 Hazard Quotient (HQ)

An estimate of risk to human health (HQ) through consumption of cereals grown in soil was calculated by the following equation:

\[
\text{Hazard Quotient (HQ)} = \frac{\text{ADD (mg/kg/day)}}{\text{RfD}_o}
\]

Where, \(\text{RfD}_o\) is the oral reference dose. \(\text{RfD}_o\) is an estimate of a daily oral exposure for the human population, which does not cause deleterious effects during a lifetime [15].

2.6 Hazard Index (HI)

To estimate the risk to human health through more than one heavy metal (HM), the hazard index (HI) was developed [16]. The hazard index is the sum of the hazard quotients for all HMs, which was calculated by the Equation below.

\[
\text{Total Chronic Hazard Index (THI)} = \sum \text{HQ}
\]

2.7 Cancer Risks

The associated dose is called the Lifetime Average Daily Dose (ADD) or Chronic Daily Intake (CDI). It was worked out for As, Cd and Pb using the equation below:

\[
\text{Incremental Lifetime Cancer Risk (ILCR)} = \text{ADD} \times \text{CSF}
\]

ADD (average daily dose of chemical, mg kg\(^{-1}\) BWday\(^{-1}\)) represents the lifetime average daily dose of exposure to the chemical. The ADD value was calculated on the basis of the equation below:

\[
\text{ADD} = \text{EDI} \times \text{EFr} \times \text{EDtot}/\text{AT}
\]

where EDI is estimated daily dose of metal via consumption cereals; EFr is exposure frequency (365 days/year); EDtot is the exposure duration 58.65 years average lifetime for Nigeria; AT is the period of exposure for non-carcinogenic effects (equal to EFr \(\times \text{EDtot}\)), and 70-year lifetime for carcinogenic effects (i.e., 70 years \(\times 365\) days/year) [15].

3. RESULTS

The mean concentrations of heavy metals in soya bean samples from different Agricultural Locations in Kwayakusar and Shani Local Government area during post and pre-harvest are as presented in Fig. 1. The mean concentrations of heavy metals from Kwayakusar Local Government agricultural locations are Mn ranged between 3.46 and 4.82 mg/kg; 3.28 and 4.66 mg/kg Fe; 0.14 and 0.52 mg/kg Ni; 0.17 and 0.23 mg/kg Co; 0.12 and 1.28 mg/kg Cu; 0.42 and 1.12 mg/kg Zn; 0.002 and 0.08 mg/kg Pb 0.07 and 0.94 mg/kg Cd; and 0.18 and 0.43 mg/kg As.

The mean concentrations of heavy metals from Shani Local Government agricultural locations are Mn ranged between 3.69 and 5.4 mg/kg; 13.07 and 17.06 mg/kg Fe; 0.27 and 0.42 mg/kg Ni; 0.22 and 0.31 mg/kg Co; 0.28 and 1.12 mg/kg Cu; 0.71 and 2.06 mg/kg Zn; 0.11 and 0.52 mg/kg Pb; 0.08 and 1.15 mg/kg Cd; and 0.02 and 0.44 mg/kg As.

The mean concentrations of heavy metals in sorghum samples from different agricultural locations in Kwayakusar and Shani Local Government areas during pre and post-harvest are as presented in Fig. 2. The mean concentrations of heavy metals from Kwayakusar Local Government agricultural locations are Mn ranged between 3.17 and 4.27 mg/kg; 3.88 and 5.79 mg/kg Fe; 0.14 and 0.55 mg/kg Ni; 0.27 and 0.37 mg/kg Co; 0.05 and 0.79 mg/kg Cu; 0.71 and 2.06 mg/kg Zn; 0.05 and 0.44 mg/kg Pb; 0.07 and 0.54 mg/kg Cd and 0.06 and 0.52 mg/kg As. The mean concentrations of heavy metals from Shani Local Government agricultural locations are Mn ranged between 3.54 and 7.48 mg/kg; 3.04 and 8.32 mg/kg Fe; 0.46 and 1.16 mg/kg Ni; 0.08 and 0.30 mg/kg Co; 0.06 and 0.08 mg/kg Cu; 0.46 and 1.90 mg/kg Zn; 0.06 and 0.23 mg/kg Pb; 0.37 and 0.50 mg/kg Cd and 0.13 and 0.60 mg/kg As.
The mean concentrations of heavy metals in maize samples from different Agricultural Locations in Kwayakusar and Shani Local Government area during post and pre-harvest are as presented in Fig. 3. The mean concentrations of heavy metals from Kwayakusar Local Government agricultural locations are Mn ranged between 0.29 and 0.56 mg/kg; 1.24 and 2.28 mg/kg Fe; 0.04 and 0.07 mg/kg Ni; 0.37 and 0.58 mg/kg Co; 0.16 and 0.24 mg/kg Cu; 0.09 and 0.40 mg/kg Zn; 0.07 and 0.13 mg/kg Pb; 0.12 and 0.03 mg/kg Cd; and 0.02 and 0.06 mg/kg As.

The mean concentrations of heavy metals from Shani Local Government agricultural locations are Mn ranged between 0.05 and 0.22 mg/kg; 0.33 and 0.92 mg/kg Fe; 0.001 and 0.05 mg/kg Ni; 0.01 and 0.45 mg/kg Co; 0.04 and 0.09 mg/kg Cu; 0.21 and 0.31 mg/kg Zn; 0.02 and 0.18 mg/kg Pb; 0.03 and 0.13 mg/kg Cd; and 0.06 and 0.12 mg/kg As.

The average daily dose (mg/kg day$^{-1}$) for heavy metals in soya beans, sorghum and maize samples from different agricultural locations of Shani and Kwayakusar Local Government areas during pre-harvest and post-harvest are as presented in Tables 1 to 3. Highest daily dose of Fe (7.53E+01) is detected in soya beans from Shani Local Government Area, while the lowest in soya beans is As(6.62E-02) from same area. For Ni the highest is 4.80E+01 in maize from Kwayakusar Local Government agricultural locations, while lowest in maize from the same area is Fe 2.35E-02. The highest average daily dose for Cu is 9.33E+02 detected in maize from Kwayakusar Local Government agricultural locations, while the lowest in maize from the same area is Fe 5.72E+00. For Zn the highest is 4.12E+03 in maize from Kwayakusar Local Government area, while the lowest Zn in the same maize from the same area is 2.16+03. Highest for Pb is 1.82E+04 in maize from Kwayakusar Local Government area and the lowest Pb in maize in the same area is 9.55E+03. The highest average daily dose for Cd is 8.01E+04 in maize from Kwayakusar Local Government area, while the lowest Cd in maize is 1.70E+02 from Kwayakusar Local Government Area. Finally, highest for As is 2.05E+05 in maize from Shani Local Government area, while lowest average daily dose of As in maize 7.70E+02 from the same area. The average daily dose of most of the heavy metals are found to be higher in Kwayakusar Local Government agricultural locations than Shani Local Government agricultural locations. The average daily dose of the metals is higher in maize compared to sorghum and soya beans.

![Fig. 1. Mean concentrations of some metals in soya beans samples during the pre-harvest and post-harvest from Kwayakusar and Shani Local Government areas](image-url)
The hazard quotient and hazard index for heavy metals via consumption of soya bean, sorghum and maize from Shani and Kwayakusar Local Government areas agricultural locations, during the pre-harvest and post-harvest are as presented in Tables 4 to 6. Highest hazard quotient of Fe (1.08E+02) is detected in soya beans from Shani Local Government Area, while the lowest in soya beans is As (1.84E+00) from same area. For Ni the highest is 2.40E+03 detected in maize from Kwayakusar Local Government locations, while the lowest Ni in maize from the same area is 5.15E+00. For Zn the highest is 1.37E+04 in maize from Kwayakusar Local Government area, while the lowest Zn in maize from the same area is 2.16E+03. Highest for Pb is 4.54E+06 in maize from Kwayakusar Local Government area and the lowest Pb in maize in
the same area is 9.74E+03. The highest hazard quotient for Cd is 8.01E+04 in maize from Kwayakusar Local Government area, while the lowest Cd in maize is 1.72E+05 from Kwayakusar Local Government Area. Finally, highest for As is 1.18E+09 in maize from Kwayakusar Local Government area, while lowest hazard quotient of As in maize 6.18E+028from the same area. The hazard quotient of most of the heavy metals is found to be higher in Kwayakusar Local Government agricultural locations than Shani Local Government agricultural locations. The hazard quotient of the metals is higher in maize compared to sorghum and soya beans.

Highest Carcinogenic risk assessment for Pb is 1.54E+02 in maize from Kwayakusar Local Government area agricultural location and the lowest Pb(6.25E-05) in sorghum from the same area. The highest Carcinogenic risk assessment for Cd is 5.05E+05 in maize from Kwayakusar Local Government area, while the lowest Cd(1.95E+00) in sorghum also from Kwayakusar Local Government Area. Highest for As is 5.30E+05 in maize from Kwayakusar Local Government area, while lowest Carcinogenic risk assessment of As is 3.13E-01 was detected in sorghum from the same area. The Carcinogenic risk assessment of the three heavy metals is found to be higher in Kwayakusar Local Government agricultural locations than Shani Local Government agricultural locations. The Carcinogenic risk assessment of the heavy metals is higher in maize compared to sorghum and soya beans.

Tables 10 and 11 present the Average Daily Dose and Oral Reference Dose (RfDo) of some heavy metals respectively.

4. DISCUSSION

4.1 Variations of Heavy Metals in the Soya Beans, Sorghum and Maize Samples

From the results of the present study, the levels of all the metals studied in the grains samples from all the agricultural locations were significantly higher during the post-harvest period when compared to pre-harvest (Figs. 1-3). The highest concentration of Mn (7.48E+00 mg/kg) was detected in sorghum, while the lowest concentration (5.00E-02 mg/kg) was observed in maize all in Shani Local Government agricultural locations. It has been reported that high level of manganese leads to the production of free radicals thereby causing several ailments with time in human body. The values of Mn are high when compared to the [17] joint safe limit of 0.3 mg/kg in some agricultural locations.

The highest concentration of Fe (17.06E+00 mg/kg) was detected in the soya beans at Shani Local Government agricultural location, while the lowest concentration (3.30E-01 mg/kg) was observed in maize also in Shani Local Government agricultural location. Iron is an essential component of several cofactors including haemoglobin and the cytochromes. Iron is a potentially toxic heavy metal. In excess, it can cause cancer, heart disease, liver disease, kidney disease and other illnesses [18]. The levels of Fe in all the soya beans and some maize and sorghum were higher than the [19] safe limit of 0.3 mg/kg in the present study.

The highest concentration of Ni (5.20E-01 mg/kg) was detected in soya beans, while the lowest concentration (1.00E-02 mg/kg) was observed in maize both in Shani Local Government agricultural locations. Foods naturally high in nickel include soya-beans, nuts and oat meals. The values of Ni were high when compared to the [19] joint safe limit of 0.1 mg/kg in some agricultural location.

For Co the highest concentration of 5.80E-01 mg/kg was detected in maize in Shani Local Government agricultural locations while the lowest concentration (1.20E-02 mg/kg) was also observed in maize in Kwayakusar Local Government agricultural locations.

The highest concentration of Cu (1.28E+00 mg/kg) was detected in the soya beans sample in Kwayakusar Local Government agricultural locations and the lowest concentration (4.40E-02 mg/kg) was observed in sorghum at Shani Local Government agricultural location. The levels of Cu in the soya beans, sorghum and maize were observed to be higher than [19] joint safe limit of 0.1mg/kg in some agricultural locations.

For Zn, the highest concentration of 2.07E+00 mg/kg was detected in the sorghum sample, while the lowest concentration (8.90E-02 mg/kg) was observed in maize sample both at Kwayakusar Local Government agricultural locations.
Table 1: Average daily dose (mg/kg day\(^{-1}\)) for heavy metals in soya beans samples from different agricultural locations in Shani and Kwayakusar Local Government Areas during pre-harvest and post-harvest

| Locations       | Fe    | Ni    | Cu    | Zn    | Pb    | Cd    | As    |
|-----------------|-------|-------|-------|-------|-------|-------|-------|
| Pre-Harvest     |       |       |       |       |       |       |       |
| Shani L.G       | 5.77E+01 | 1.17E+00 | 1.25E+00 | 3.14E+00 | 4.83E-01 | 3.64E-01 | 6.62E-02 |
| Kwayakusar L.G  | 1.45E+01 | 6.01E-01 | 5.20E-01 | 1.87E+00 | 3.45E-01 | 3.13E-01 | 7.92E-02 |
| Total ADD       | 7.22E+01 | 1.77E+00 | 1.77E+00 | 5.01E+00 | 8.28E-01 | 6.77E-01 | 1.45E-01 |
| Post-Harvest    |       |       |       |       |       |       |       |
| Shani L.G       | 7.53E+01 | 1.84E+00 | 4.94E+00 | 2.88E+00 | 2.30E+00 | 5.06E+00 | 1.95E+00 |
| Kwayakusar L.G  | 2.06E+01 | 2.29E+00 | 5.65E+00 | 4.93E+00 | 3.13E-01 | 7.35E-03 | 1.91E+00 |
| Total ADD       | 9.59E+01 | 4.13E+00 | 1.06E+01 | 7.81E+00 | 2.31E+00 | 9.20E+00 | 3.86E+00 |

Table 2. Average daily dose (mg/kg day\(^{-1}\)) for heavy metals in sorghum samples from different agricultural locations in Shani and Kwayakusar Local Government Areas during pre-harvest and post-harvest

| Locations       | Fe    | Ni    | Cu    | Zn    | Pb    | Cd    | As    |
|-----------------|-------|-------|-------|-------|-------|-------|-------|
| Pre-harvest     |       |       |       |       |       |       |       |
| Shani L.G       | 1.34E+01 | 5.12E+00 | 2.54E-01 | 2.01E+00 | 2.80E-01 | 1.64E+00 | 5.73E-01 |
| Kwayakusar L.G  | 1.71E+01 | 5.95E-01 | 3.32E-01 | 3.12E-01 | 2.35E-01 | 3.10E-01 | 2.09E-01 |
| Total ADD       | 3.05E+01 | 5.72E+00 | 5.86E-01 | 5.13E+00 | 5.15E-01 | 1.95E+00 | 7.82E-01 |
| Post-harvest    |       |       |       |       |       |       |       |
| Shani L.G       | 3.67E+01 | 2.04E+00 | 3.68E-01 | 8.36E+00 | 1.01E+00 | 2.19E+00 | 2.65E+00 |
| Kwayakusar L.G  | 2.56E+01 | 2.41E+00 | 3.49E+00 | 9.11E+00 | 1.92E+00 | 2.40E+00 | 2.28E+00 |
| Total ADD       | 6.23E+01 | 4.45E+00 | 3.86E+00 | 1.75E+01 | 2.93E+00 | 4.59E+00 | 4.93E+00 |

Table 3. Average daily dose (mg/kg day\(^{-1}\)) for heavy metals in maize samples from different agricultural locations in Shani and Kwayakusar Local Government Areas during pre-harvest and post-harvest

| Locations       | Fe    | Ni    | Cu    | Zn    | Pb    | Cd    | As    |
|-----------------|-------|-------|-------|-------|-------|-------|-------|
| Pre-harvest     |       |       |       |       |       |       |       |
| Shani L.G       | 2.35E-02 | 1.05E-01 | 2.00E+00 | 9.05E+00 | 3.90E+01 | 1.70E+02 | 7.70E+02 |
| Kwayakusar L.G  | 5.72E+00 | 2.52E+01 | 4.90E+02 | 2.16E+03 | 9.55E+03 | 4.21E+04 | 1.86E+05 |
| Total ADD       | 5.74E+00 | 2.53E+01 | 4.92E+02 | 2.17E+03 | 9.59E+03 | 4.23E+04 | 1.87E+05 |
| Post-harvest    |       |       |       |       |       |       |       |
| Shani L.G       | 6.35E+00 | 2.80E+01 | 5.50E+02 | 2.40E+03 | 1.10E+04 | 4.65E+04 | 2.05E+05 |
| Kwayakusar L.G  | 1.09E+01 | 4.80E+01 | 9.33E+02 | 4.12E+03 | 1.82E+04 | 8.01E+04 | 3.53E+03 |
| Total ADD       | 1.73E+01 | 7.60E+01 | 1.48E+03 | 6.52E+03 | 2.92E+04 | 1.27E+05 | 2.09E+05 |
Table 4. Hazard quotient and hazard index (mg/kg day\(^{-1}\)) of non-carcinogenic heavy metals via consumption of soya beans from agricultural locations in Shani and Kwayakusar Local Government Areas during the pre-harvest and post-harvest.

| Locations    | Fe     | Ni     | Cu     | Zn     | Pb     | Cd     | As     |
|--------------|--------|--------|--------|--------|--------|--------|--------|
| **Pre-Harvest** |        |        |        |        |        |        |        |
| Shani L.G    | 8.24E+01 | 5.86E+01 | 3.11E+01 | 1.05E+01 | 1.21E+02 | 3.64E+02 | 2.21E+02 |
| Kwayakusar L.G | 2.07E+01 | 3.00E+01 | 1.30E+01 | 6.24E+00 | 8.64E+01 | 3.13E+02 | 2.65E+03 |
| **HI**       | 1.03E+02 | 8.86E+01 | 4.14E+01 | 1.67E+01 | 2.07E+02 | 6.77E+02 | 2.87E+03 |
| **Post-Harvest** |        |        |        |        |        |        |        |
| Shani L.G    | 1.08E+02 | 9.20E+01 | 1.23E+02 | 9.60E+00 | 5.76E+02 | 5.06E+03 | 6.47E+03 |
| Kwayakusar L.G | 2.94E+01 | 1.15E+02 | 1.41E+02 | 1.64E+01 | 1.84E+00 | 4.14E+03 | 6.37E+03 |
| **HI**       | 1.37E+02 | 2.07E+02 | 2.64E+02 | 2.60E+01 | 5.78E+02 | 9.20E+03 | 1.28E+04 |

Table 5. Hazard quotient and hazard index (mg/kg day\(^{-1}\)) of non-carcinogenic heavy metals via consumption of sorghum from Shani and Kwayakusar Local Government Areas Agricultural Locations, Borno State, Nigeria during the pre-harvest and post-harvest.

| Locations    | Fe     | Ni     | Cu     | Zn     | Pb     | Cd     | As     |
|--------------|--------|--------|--------|--------|--------|--------|--------|
| **Pre-Harvest** |        |        |        |        |        |        |        |
| Shani L.G    | 1.91E+01 | 2.56E+02 | 6.35E+00 | 6.71E+00 | 7.01E+01 | 1.64E+03 | 1.91E+03 |
| Kwayakusar L.G | 2.45E+01 | 2.98E+01 | 5.81E+00 | 1.04E+01 | 5.87E+01 | 3.10E+02 | 6.96E+02 |
| **HI**       | 4.36E+01 | 2.86E+02 | 1.22E+01 | 1.71E+01 | 1.29E+02 | 1.95E+03 | 2.61E+03 |
| **Post-Harvest** |        |        |        |        |        |        |        |
| Shani L.G    | 5.24E+01 | 1.02E+02 | 9.22E+00 | 2.79E+01 | 2.51E+02 | 2.19E+03 | 8.83E+03 |
| Kwayakusar L.G | 3.65E+01 | 1.21E+02 | 8.74E+01 | 3.04E+01 | 4.80E+02 | 2.40E+03 | 7.60E+03 |
| **HI**       | 8.89E+01 | 2.23E+02 | 9.66E+01 | 5.83E+01 | 7.31E+02 | 4.59E+03 | 1.64E+04 |

Table 6. Hazard quotient and hazard index (mg/kg day\(^{-1}\)) of non-carcinogenic heavy metals via consumption of maize from Shani and Kwayakusar Local Government Areas Agricultural Locations, Borno State, Nigeria during the pre-harvest and post-harvest.

| Locations    | Fe     | Ni     | Cu     | Zn     | Pb     | Cd     | As     |
|--------------|--------|--------|--------|--------|--------|--------|--------|
| **Pre-Harvest** |        |        |        |        |        |        |        |
| Shani L.G    | 3.33E-02 | 5.15E+00 | 5.01E+01 | 2.95E+01 | 9.74E+03 | 1.72E+05 | 2.52E+06 |
| Kwayakusar L.G | 8.17E+00 | 1.26E+03 | 1.23E+04 | 7.21E+03 | 2.38E+06 | 4.21E+07 | 6.18E+08 |
| **HI**       | 8.20E+00 | 1.27E+03 | 1.24E+04 | 7.24E+03 | 2.39E+06 | 4.23E+07 | 6.21E+08 |
| **Post-Harvest** |        |        |        |        |        |        |        |
| Shani L.G    | 9.09E+00 | 1.41E+03 | 1.36E+04 | 8.02E+03 | 2.66E+06 | 4.68E+07 | 6.88E+08 |
| Kwayakusar L.G | 1.56E+01 | 2.49E+03 | 2.34E+04 | 1.37E+04 | 4.52E+06 | 8.01E+07 | 1.18E+09 |
| **HI**       | 2.47E+01 | 3.81E+03 | 3.70E+04 | 2.17E+04 | 7.20E+06 | 1.27E+08 | 1.87E+09 |
### Table 7. Carcinogenic risk assessment (mg/kg day\(^{-1}\)) of some heavy metals in soya beans from Shani and Kwayakusar Local Government Areas of Borno State, Nigeria during the pre-harvest and post-harvest

| Locations       | Pb          | Cd          | As          |
|-----------------|-------------|-------------|-------------|
| Pre-Harvest     |             |             |             |
| Shani L.G       | 4.11E-03    | 2.29E+00    | 9.91E-02    |
| Kwayakusar L.G  | 2.93E-03    | 1.97E+00    | 1.19E+00    |
| ∑ILCR           | 7.04E-03    | 4.26E+00    | 1.29E+00    |
| Post-Harvest    |             |             |             |
| Shani L.G       | 1.96E-02    | 3.19E+01    | 2.91E+00    |
| Kwayakusar L.G  | 6.25E-05    | 2.61E+01    | 2.87E+00    |
| ∑ILCR           | 1.97E-02    | 5.80E+01    | 5.78E+00    |

### Table 8. Carcinogenic risk assessment (mg/kg day\(^{-1}\)) of some heavy metals in sorghum from Shani and Kwayakusar Local Government Areas of Borno State, Nigeria during the pre-harvest and post-harvest

| Locations       | Pb          | Cd          | As          |
|-----------------|-------------|-------------|-------------|
| Pre-harvest     |             |             |             |
| Shani L.G       | 2.38E-03    | 1.03E+01    | 1.72E+00    |
| Kwayakusar L.G  | 2.00E-03    | 1.95E+00    | 3.13E-01    |
| ∑ILCR           | 4.38E-03    | 1.23E+01    | 2.03E+00    |
| Post-harvest    |             |             |             |
| Shani L.G       | 8.53E-03    | 1.38E+01    | 3.79E+00    |
| Kwayakusar L.G  | 1.63E-02    | 1.51E+01    | 3.42E+00    |
| ∑ILCR           | 2.48E-02    | 2.89E+01    | 7.21E+00    |

### Table 9. Carcinogenic risk assessment (mg/kg day\(^{-1}\)) of some heavy metals in maize from Shani and Kwayakusar Local Government Areas of Borno State, Nigeria during the pre-harvest and post-harvest

| Locations       | Pb          | Cd          | As          |
|-----------------|-------------|-------------|-------------|
| Pre-harvest     |             |             |             |
| Shani L.G       | 3.31E-01    | 1.08E+03    | 1.14E+03    |
| Kwayakusar L.G  | 8.11E+01    | 2.65E+05    | 2.78E+05    |
| ∑ILCR           | 8.14E+01    | 2.66E+05    | 2.79E+05    |
| Post-harvest    |             |             |             |
| Shani L.G       | 9.02E+01    | 2.95E+05    | 3.10E+05    |
| Kwayakusar L.G  | 1.54E+02    | 5.05E+05    | 5.30E+05    |
| ∑ILCR           | 2.44E+02    | 8.00E+05    | 8.40E+05    |

### Table 10. Average daily dose of some heavy metals

| Heavy metal | Integrated risk information system [15] |
|-------------|----------------------------------------|
| Fe          | 4E-01                                  |
| Zn          | 40E-01                                 |
| Cu          | 10E-01                                 |
| Pb          | 2.40E-01                               |
| Cd          | 6.40E-02                               |
| Mn          | 11E-01                                 |
| Cr          | 1.05E-02                               |

### Table 11. Oral reference dose (RfDo)

| Heavy metal | RfDo (mg kg\(^{-1}\) day\(^{-1}\)) |
|-------------|-----------------------------------|
|             | Integrated Risk Information System [15] | [19] |
| Fe          | -                                  | 7.00E-01 |
| Zn          | -                                  | 3.00E_01 |
| Cu          | -                                  | 4.00E-02 |
| Pb          | 1.00E-03                           | 4.00E-03 |
| Cd          | -                                  | 1.00E-03 |
| Mn          | -                                  | 1.40E-02 |
| Cr          | 1.50E+00                           | 1.50E+00 |
Zinc is the least toxic and an essential element in human diet as it is required to maintain the functioning of the immune system. Zinc deficiency in the diet may be highly detrimental to human health than too much zinc in the diet. The recommended dietary allowable concentration for zinc is 15 mg/day for men and 12 mg/day for Women [20] as cited by [21]. Soya beans, maize and sorghum that grow on heavy metal contaminated soils can accumulate high concentrations of zinc to cause serious health risk to the soya beans consumers. The zinc content was found to be lower than the [17] safe limit of 3.00 mg/kg in some agricultural locations.

For Pb from the agricultural locations the highest concentration is 5.23E-01 mg/kg in soya beans in Shani Local Government agricultural locations, while the lowest concentration (2.00E-02 mg/kg) was also observed in soya beans from Kwayakusar Local Government agricultural location. Lead is a serious cumulative body poison which enters into the body system through air, water and food and cannot be removed by washing fruits, seed and vegetables [22]. The high levels of lead in some plants may probably be attributed to pollutants in farm soil or due to pollution from the highways traffic, application of fertilizer [23]. Lead pollution has been shown to be commensurate with population/vehicular density and agricultural practice. One possible explanation for this situation is that the Pb uptake can be promoted by the pH of soil and the levels of organic matter. Lead is a toxic element that can be harmful to plants, although plants usually show ability to accumulate large amounts of lead without visible changes in their appearance or yield [21]. In many plants, Pb accumulation can exceed several hundred times the threshold of maximum level permissible for human consumption [24]. The introduction of Pb into the food chain may affect human health and thus, studies concerning Pb accumulation in vegetables have increasing importance. Pb values in all soya beans studied were higher when compared to the [19] joint safe limit of 0.01 mg/kg in some agricultural locations.

The highest concentration of Cd (1.15E+00 mg/kg) was detected in soya beans sample in Shani Local Government agricultural locations while the lowest concentration (2.80E-02 mg/kg) was observed in maize sample in Kwayakusar Local Government agricultural locations. There has been report that cadmium is a highly mobile metal, easily absorbed by the plants through root surface and moves to stem, seed and leaf of the plants. [22] and [24] reported that there is a direct relation between the levels of presence of cadmium in the root zone and its absorption by plant. The contents of cadmium reported in some studied agricultural locations in this study were observed to be higher than the [19] safe limit of 0.02 mg/kg.

The highest concentration of As (5.17E-01 mg/kg) was detected in the sorghum at Kwayakusar Local Government agricultural location, while the lowest concentration (1.50E-02 mg/kg) was also observed in maize at Kwayakusar Local Government agricultural location.

### 4.2 Average Daily Dose

The Daily cereal consumption was obtained through estimation of average consumption of cereals (soya bean, sorghum and maize) per person per day for human. The degree of toxicity of heavy metal to human being depends upon their daily intake [25]. Average daily dose is a function of body weight and intake. The ADD estimated for all the study area is as shown in Table 1 to 3.

In the present study, the highest ADD value for Ni is 4.80E+01 mg/kg per day which was detected in maize in Kwayakusar Local Government area, and the lowest (1.05E-01 mg/kg per day) also in so maize in Shani Local Government agricultural location. The highest daily dose of Fe was estimated as 7.53E+01 mg/kg per day in sorghum samples from Shani Local Government, while the lowest daily dose of Fe was estimated as 2.35E-02 mg/kg per day in maize sample also from Shani Local Government area. The lowest ADD for As was estimated as 6.62E-02 mg/kg per day in sorghum samples from Shani Local Government, while the highest value of 2.05E+05 mg/kg per day in maize samples also from Shani Local Government. The lower ADD values in all the cereal samples studied were lower than that of 0.008 and 0.052 mg/kg per day by [26] and [27] respectively. [28] recorded higher ADD values for heavy metals than tolerable daily intake limits. In all the study area, the estimated average daily intakes of heavy metals through the consumption of cereals was higher than the tolerable daily intake limit set by the [15] (Table 10). The observed results show that, there is risk upon the consumption of the study cereals.
4.3 Estimation of Hazard Quotient (HQ)

The estimation of hazard quotient and hazard index (HQ) values was calculated on the basis of the oral reference dose. Oral reference doses (RfDo) for heavy metals as presented in Table 11 [19]. From the result obtained, in all the sample locations, the HQ values of all heavy metals, in all cereal samples were all above one (1) Table 4 to 6. When HQ exceed one (1), there is concern for health effect [29]. The lowest HQ value of 5.81E+00 for Cu in sorghum in Kwayakusar Local Government area and the highest HQ of 1.18E+09 for As in maize samples also in Kwayakusar Local Government agricultural location was higher than the HQ values of one (1), while for soya beans, the lowest and highest HQ value of 1.84E+00 for Pb from Kwayakusar Local Government area and 2.21E+02 for As from Shani Local Government area exceeded the HQ value of (1) one. [28] also found HQ in Spinach as high as 5.3 E-00. The high HQ values for all the metal studied in the cereal samples had greatest potential to pose health risk to the consumers. The results further indicated that the population might be probably exposed to some potential health risk through the intake of of heavy metals via consuming the cereals. Higher HQ for Pb were also reported by [30] in vegetables collected from a Huludao Zinc Plant in Huludao city, China; and in vegetables from Pb and Sb smelter in Nanning, China as reported by [31]. In the present study, all heavy metals might be responsible for causing risk to the population that consumed the cereals as the value of HQ was above 1 for all the cereals from the study area.

4.4 Hazard Index (HI)

An index of risk called hazard index (HI) for residents of ingesting of heavy metals by consuming cereals grown in the study areas were calculated by summation of HQ of all heavy metals for each cereal (Tables 4 to 6). In the present study the highest HI of heavy metals was found in maize samples from Kwayakusar Local Government with a value of 1.87E+09 for As, whereas the lowest HI was found in soya beans also from same area with a value of 8.20E+00 for Fe. HI values of heavy metals for all the cereals were between 8.20E+00 and 1.87E+09. All of these values were more than one (1), indicating that there was risk from the intake of these cereals. [29] and [32] also recorded minimum contribution of heavy metals to aggregated risk via consumption of vegetables in Kunshan and Tianjin, China.

4.5 Cancer Risk Assessment

Cancer risks were computed as 5.30E+05 for highest and 6.25E-05 for lowest chances for the study cereals respectively (Tables 7 to 9). These risk values indicate that consumption of cereals from Kwayakusar Local Government area would result in an excess of 2 cancer cases per 1000000 people, while consumption of cereals would result into an excess of 2 cancer cases per 10,000 people [33]. The risk of developing cancer as a result of consuming soya beans, Sorghum and maize showed significant difference (p > 0.05). Compared to all the metals study, As and Cd was predominant contaminant contributing more of the ILCR in soya beans, Sorghum and maize respectively. In general, EPA considers excess cancer risks that are below about 1chance in 1,000,000 (1.00E-06) to be so small as to be negligible, and risks above 1 in 10,000 (1×10^{-4}) to be sufficiently large that some sort of remediation is desirable. An ILCR greater than one in ten thousand (ILCR > 10^{-3}) is benchmark for gathering additional information whereas 1/1000 or greater (ILCR > 10^{-3}) is moderate and should be given high priority as a public health concern [34]. Ar, Cd, Pb and Cr are classified by the International Agency for Research on Cancer (IARC) as being carcinogenic [35]. Chronic exposure to low doses of As, Cd and Pb could therefore result into many cancers [36,37].

The average daily dose for the heavy metals from soya beans, sorghum and maize was above the tolerable daily intake. The probability of an individual developing cancer over a lifetime as a result of exposure to heavy metals through consumption of cereals was higher than acceptable risk levels (ILCR > 10^{-4}). Values of HQ for the individual metals showed potential health risk for humans due to the consumption of the study cereals. In addition, hazard indices due to the combined non-cancer effects of all the metals considered in the study were >1. Hence, consumption of the study cereals from the study area is a health risk with respect to Pb, Cd and As, and should be given higher priority as a public health concern.

5. CONCLUSION

All the heavy metals studied in soya beans and cereal samples were detected in all the agricultural locations in Shani and Kwayakusar Local Government Areas. Fe and Mn are found to dominant in both the soil soya bean and cereal.
samples. The concentrations of all the studied metals in cereal samples from were higher than the WHO/FAO safe limit of 0.02 mg/kg. The levels of all the heavy metals studied in all the agricultural locations were higher during the post-harvest, when compared to pre-harvest. The average daily dose for the heavy metals from soya beans, sorghum and maize were above the tolerable daily intake. The probability of an individual developing cancer over a lifetime as a result of exposure to heavy metals through consumption of cereals from the study area is a health risk with respect to Pb, Cd and As, and should be given higher priority as a public health concern.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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