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Nutrient Interaction and Health Risk Assessment of Cereal Grains on Nigerian's Markets

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HIGHLIGHTS

- Essential elements in Nigerian's grains were highly bioavailable *in vitro* despite the presence of phytate and oxalate.
- Levels of minerals overload in some of the cereals were not significant to cause any toxicological health risk.
- Cancer risk values of the grains were at acceptable risk levels for both adults and children.

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Acronyms and abbreviations
CR=Cancer Risk
EDI=Estimated Daily Intake
ESM=Electronic Supplementary Material
HI=Hazard Index
HQ=Hazard Quotient
MSI=Mineral Safety Index
TCR=Total Cancer Risk

ABSTRACT

Background: Cereals are the most staple foods in human diet and the main components of the daily diet. This work was designed to determine the level of essential and non-essential elements, the *in vitro* bioavailability, interrelationship, and associated health risk in consumed cereal grains in Nigeria to assess their safety and wholesomeness.
Methods: The contents of phytate, oxalate, and some major-, trace- and potentially toxic elements were determined in 36 samples of barley, maize, millet, rice, sorghum, and wheat marketed in Nigeria.
Results: The data showed variable significant (p<0.05) levels of elements, phytate, and oxalate in the cereals but they were below European commission maximum permissible limits. Estimated daily intakes (EDIs) of elements in the cereals were all below maximum permissible limits set by European Food Safety Authority (EFSA). Hazard Quotient (HQ) and Hazard Index (HI) values, though higher in children than adults, were less than one except in wheat and sorghum. The incremental lifetime Cancer Risk (CR) and Total Cancer Risk (TCR) values were below the threshold limit.
Conclusion: This study revealed that barley, maize, millet, rice, sorghum, and wheat available in Nigeria markets contain varying quantities of essential elements, potentially toxic elements, and antinutrients.

Introduction

Plants-based foods are cheap and provide quality nutrients which are accessible to larger populations especially in developing countries (Pirsaheb et al., 2015). Developing countries such as Nigeria depend mostly on cereal

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and legume grains as a cheap source of human and animal diets since they are rich sources of macro- and micro- nutrients (Prasanthi et al., 2017). Currently, cereal grains are the most popular agricultural products consumed in different processed forms because of their nutritive components (Huang et al., 2013). These cereals include barley, which ranks fifth among field crops in grain production in the world after maize; wheat; rice; and soybean.

Elements taken up by plants and incorporated into edible parts may be essential or non-essential to the plants and animals which feed on them. Essential elements may be required in large (macro) or trace (micro) quantities to serve one or more functions in the body (Ajala et al., 2020; Institute of Medicine, 2001; Obasi et al., 2020). Although, mineral elements are essentially required for healthy growth and development, their deficiency or excessive intake present diseases that vary from one element to another (McDowell, 2003). Non-essential elements also called potential toxic elements are elements that have no beneficial effects on the healthy growth and development of humans and animals (Ajala et al., 2020; McDowell, 2003). They cause numerous toxicity effects ranging from non-carcinogenic to carcinogenic toxicities depending on the elements involved (ATSDR, 2018). Potential toxic elements are continuously being introduced into agricultural lands in large quantities from anthropogenic sources which include without limitto fertilizers and agrochemicals used for crop protection purposes and atmospheric contaminant deposits from rapidly growing urban and industrial areas (Pirsaheb et al., 2015).

These contaminants make the quality of plant-based foods, especially cereals to become a serious worldwide health threat (Ali et al., 2020; Compaore et al., 2019; Mao et al., 2019; Šukalić et al., 2018; Wang et al., 2019). Mineral and potentially toxic elements are non-biodegradable and tend to persist in cells where they interact with each to elicit beneficial or toxicological effects (Ali et al., 2020; Compaore et al., 2019). The interaction or interrelationship of elements from food sources in animal or human cells may produce synergistic or antagonistic effects. These effects lead (Pb) to alterations in normal physiological and biochemical roles of cells symptomatic as deficiency or overloading effects of the elements involved (Adeyeye et al., 2012; Ajala et al., 2019; Institute of Medicine, 2001; McDowell, 2003). The level, bioavailability, nature, and mechanisms of action of elements determine their toxicological effects (Flora et al., 2012).

The level and bioavailability of elements in plants-based foods is strongly affected by the amount of some inherent anti-nutritional factors present in the plants-based foods (Adubiaro et al., 2011). Phytate and oxalate are important constituents of cereals and other plants which are capable of chelating divalent cationic minerals like calcium (Ca), iron (Fe), magnesium (Mg), and zinc (Zn) (Abdelrahaman et al., 2007; Ajala et al., 2020; Gemede, 2020). The presence of phytate (myoinositol 1,2,3,4,5,6-hexakis-phosphate) in the diet chelates the dietary minerals, such as Ca and Zn, and negatively affects their uptake thereby inducing dietary elemental deficiency (Ajala et al., 2020; Gemede, 2020; Gemede and Ratta, 2018). Oxalate is a salt formed of oxalic acid (HOOC-COOH). Higher content of oxalate can bind to minerals such as Ca, Mg, sodium (Na), and potassium (K) present in food to form soluble or insoluble salts, thereby rendering them unavailable for normal physiological and biochemical roles (Gemede and Ratta, 2018). The oxalate salts formed, for example, calcium oxalate; may precipitate in soft tissues such as in kidneys thereby causing kidney stones (Gemede and Ratta, 2018).

Currently, there is high dependence on cereal foods, especially in the formulation of complementary foods for children and different staple foods for adults as they were reported to contain nutrients (such as carbohydrates, proteins, lipids, vitamins), and contaminants (Jākobsone et al., 2015; Winiarska-Mieczan et al., 2020). They also contain essential and non-essential elements and anti-nutritional factors, whose level depends on the soil as growth media, the genetic make-up, and the level of contamination from the field to the consumers (Ali et al., 2020; Jākobsone et al., 2015; Pirsaheb et al., 2015; Šukalić et al., 2018; Wang et al., 2019). The high demand for cereal by all age groups and the fact that they can accumulate contaminants makes it very necessary to continuously assess their nutritional and toxicological potentials. Therefore, this work was designed to determine the level of essential and non-essential elements, the *in vitro* bioavailability, interrelationship, and associated health risk in commonly consumed cereal grains in Nigeria to assess their safety and wholesomeness.

Materials and methods

Collection of samples

Six cereal grains: barley (*Hordeum vulgare* L.), millet (*Eleusine coracona)*, maize (*Zea mays* L.), rice (*Oryza sativa* L.), sorghum (*Sorghum bicolor* L. Moench), and wheat (*Triticum aestivum*) were obtained from consumer shops between October and November 2021, in Eke-Aba main market, Abakaliki, Nigeria. Six different representative samples from each kind of the cereals were taken to the Plant Ecology Research Unit of the Department of Science Laboratory Technology, Akanu Ibiam Federal Polytechnic Unwana, Nigeria, where they were identified and authenticated. The grains were washed with deionized water and oven-dried at 65 °C for 6 h. The dried samples were ground into fine powdered flours using an electric grain mill (Wonder Mill® WM 2,000, US). The fine flours were packed into airtight polythene bags, labelled, and stored at ambient condition until required for digestion.

Digestion, calibration, and analysis of samples

The samples under study were first digested using wet digestion method (Ajala et al., 2020). Briefly, approximately 1.0 g of each sample was weighed (LARK LA114, UK) into individual tarred digestion vessels. Acid mixture of nitric acid (HNO_3; 69.5%), sulfuric acid (H_2SO_4; 98%), and perchloric acid ($HClO_4$; 70%) in ratio 5:1:1 were added, respectively. The round bottom flask was fitted to a reflux condenser and heated on a Kjeldahl apparatus hot plate at a temperature of 80 °C until colourless solution was obtained. The digest was allowed to stand and cool to the room temperature. The mixture was then diluted with 10 ml of double-distilled deionized water and filtered with Whatman filter paper No. 42 into a 50 ml volumetric flask. The round bottom flask was further rinsed with 5 ml of deionized water and added to the filtrate. For each sample, the digestion was done in triplicate. A mixture of 11 ml of HNO_3, 2.2 ml of H_2SO_4, and 2.2 ml of $HClO_4$ were also similarly digested as blank following the same procedure as for the samples. The standard solutions for all the elements under study were prepared in 5 different concentrations to obtain a calibration curve by diluting stock standard solutions of concentration 1,000 mg/dm^3.

The levels of each element in all the samples were determined as described by Ajala et al. (2020) using a spectrometer (Atomic Absorption Spectroscopy (AAS) 7,000, Shimadzu, Japan) with Graphite Furnace atomization (GF-AAS) for copper (Cu; 324.9 nm), cadmium (Cd; 228.8 nm), chromium (Cr; 267.7 nm), and Pb (283.3 nm); with Flame atomization (FAAS) for Ca (228.8 nm), Mg (285.3 nm), manganese (Mn; 279.4 nm), Fe (248.3 nm), and Zn (213.9 nm); and the volatile elements, arsenic (As; 189.0 nm), and selenium (Se; 190.0 nm) with hydride generation coupled with AAS after the operating conditions were optimized at the maximum signal intensity of the instrument. Na and K were determined at 589 nm and 766 nm, respectively with Flame Emission Photometer (PFP7, Jenway) using analytical grade sodium chloride (NaCl) and potassium chloride (KCl) as standards, respectively. The phosphovanadomolybdate method of AOAC (2000) was used to determine phosphorus content in the samples at 660 nm with an ultraviolet/visible spectrophotometer (V-730, Analytik Jena Spectrocord, Germany) using potassium dihydrogen phosphate (KH_2PO_4) as a standard. Detailed calibration method and results are presented in Electronic Supplementary Material (ESM) Table 1.

The phytate content was determined as described by Hailu and Addis (2016). The absorbance was measured at 500 nm using UV-visible spectrophotometer (V-730, Analytik Jena Spectrocord Model, Germany). The oxalate contents of the grain samples were determined using titration method as outlined by Inuwa et al. (2011).

Quality control and method validation

The chemicals used were of ultra-pure analytical grade (British Drug House Limited, UK) and were checked for possible trace metal contamination. Double distilled deionized water was used throughout the experimental work. All the glassware were thoroughly washed, rinsed, and dried before use. The accuracy of the measurements was determined by analyzing spiked samples and the percentage recovery ranged from 99.7 (K) to 100.3% (Cu). The precision of the measurements was expressed as a relative standard deviation (RSD); the percent RSD was less than 5%. The Limit of Detection (LOD) was estimated by digestion 5 analytical blanks following the same procedure used for the samples. Triplicate readings were performed for each element and the pooled standard deviations were calculated. The method limits of detection were 0.01 mg/kg for Cu, Mn, Se, Cr, Nickel (Ni), and As; 0.02 mg/kg for Ca, Mg, Zn, Fe, Pb, and Cd; 0.03 and 0.04 mg/kg, respectively for Na and K. The correlation coefficients (R^2) of all the calibration curves were found to be ≥0.9974. Detailed validation results are presented in ESM Table 2.

Data analysis

-Minerals ratios

The mineral ratios, Ca/P, Ca/K, Ca/Mg, Na/K, Na/Mg, Zn/Cu, Fe/Cu, and the milliequivalent (mEq) ratio of [K/(Ca+Mg)] were computed according to Watts (2010). Computation of mEq ratio of elements was done by first computing the mEq value of an element as shown in equation (1):

$$\text{mEq of K}=\frac{(\text{mg of K}) \times (\text{valence of K})}{\text{molecular weight of K}} \quad (1)$$

The valence of K, Ca, and Mg were 1, 2, and 2, respectively while the molecular weights were 39.10, 40.08, and 24.31, respectively.

-Mineral bioavailability

Mineral bioavailability depicted by molar ratios: [Phytate]:[Zn], [Phytate]:[Fe], [Ca]:[Phytate], [Ca]:[Oxalate], and [Ca][Phytate]:[Zn] values were calculated according to the method of Gemede (2020). Computation of molar ratios was done according to the example in equations 2 and 3.

Molar ratio of [phy]/[Zn]=(mg of phy)/(MW of phy)÷(mg of Zn)/(AW of Zn) (2)

Molar ratio of [Ca][phy]/[Zn]=(mol/kg Ca)×(mol/kg phy)/(mol/kg Zn) (3)

The atomic weight of Zn and Fe were 65.38, 55.85 g/mol, respectively while the Molecular Weight (MW) of phytate and oxalate were 660.04 and 88.02 g/mol, respectively.

-Mineral Safety Index (MSI)

The MSI was calculated according to the method outlined by Adeyeye et al. (2012) for minerals that have established standard safety values. The computed values were compared with MSI standard values from tables to obtain a difference which is used to predict the safety of the mineral. The calculated value of MSI was obtained using equation (4).

$$MSI_{cv} = \frac{MSI_{stv}}{RAI} \times C_{min} \quad (4)$$

In equation (4), MSI_{stv} is the MSI established standards from tables, MSI_{cv} is the MSI calculated values, RAI is the Recommended Adult Intake established standard from tables and C_{min} is the concentration of the minerals in the samples. If the difference (D)=(MSI_{stv}–MSI_{cv}) positive, it means that the mineral is moderate in the sample considered but if the value is negative, it implies mineral overloading (Hathcock, 2014; Institute of Medicine, 2001). The MSIstv values for Ca, Na, Mg, Phosphorus (P), Zn, Fe, Cu, Mn, and Se were respectively, are 10, 48, 15, 10, 33, 6.7, 33, 7.5, and 0,462 while the established standard RAI for listed elements were 1,200, 500, 400, 1,200, 15, 15, 3, 5, and 0.07, respectively.

-Estimated Daily Intakes (EDI)

The EDI of element which is the average estimate of daily elemental loading into the body system of a specified body weight of a consumer (Wcisło et al., 2016) was computed using equation (5) as outlined in Rahman and Islam (2019).

$$EDI=\frac{F_{ingestion} \times C_{element}}{BW_{average}} \times C_{factor} \quad (5)$$

In equation (5); $C_{element}$ is the measured elemental content in the grains (mg/kg), $F_{ingestion}$ is the daily food ingestion rate of the grains (kg/person-day), C_{factor} is the conversion factor from fresh to dry weight=0.085 (Khan et al., 2017; Obasi et al., 2020) and $BW_{average}$ is the average body weight, 70 kg for adult and 15 kg for children (Magna et al., 2018; Obasi et al., 2020). $F_{ingestion}$ =0.0061, 0.232, 0.15, 0.1984, 0.527, and 0.53151 kg/person-day (for children) and 0.0061, 0.345, 0.37789, 0.3892, 0.527, and 0.53151 kg/person-day (for adults) in barley, maize, millet, rice, sorghum, and wheat, respectively (Baghaie and Aghili, 2019; El-Hassanin et al., 2020; Islam et al., 2015; Satpathy et al., 2014; Yeganeh et al., 2012).

-Hazard Quotient (HQ) and Hazard Index (HI)

The HQ which is the chronic threat assessment of a specific element otherwise known as non-carcinogenic health risk and HI, which is the cumulative effect of the elements, were calculated using equations (6) and (7), respectively.

$$HQ=EDI/R_fD \quad (6)$$

$$HI=\sum (HQ_1+HQ_2 + HQ_3 \dots \dots \dots + HQ_n) \quad (7)$$

Where, R_fD is the reference dose of toxic element via oral ingestion and 1, 2, 3 n, represents the individual element whose HQ was computed. $R_fD=3.0\times10^{-1}$, 7.0×10^{-1}, 4.0×10^{-2}, 1.4×10^{-1}, 5.0×10^{-3}, 1.5×10^{0}, 2.0×10^{-2}, 3.5×10^{-3}, 1.0×10^{-3}, and 3.0×10^{-4} mg/kg-day for Zn, Fe, Cu, Mn, Se, Cr, Ni, Pb, Cd, and As, respectively (El-Hassanin et al., 2020; Janoska and Gruszecka-Kosowska, 2020; Khan et al., 2017). Humans are safe if HQ or HI<1 (Baghaie and Aghili, 2019; Islam et al., 2015; Yeganeh et al., 2012).

-Incremental lifetime Cancer Risk (CR) and Total Cancer Risk (TCR)

The CR and TCR as a result of cumulative exposure risk of multiple carcinogenic toxic elements in the study were calculated using equations (8) and (9), respectively (El-Hassanin et al., 2020, Obasi et al., 2020).

$$\text{Incremental lifetime } CR=EDI x C_sf \quad (8)$$

$$TCR=\sum [CR(Pb)+CR(As)] \quad (9)$$

C_sf is the carcinogenic slope factor (mg/kg-day)$^{-1}$ of toxic elements via oral ingestion, given as 8.5×10^{-3} and 1.5×10^{0} (mg/kg-day)$^{-1}$ for Pb and As, respectively (El-Hassanin et al., 2020; Khan et al., 2017). At present, no oral carcinogenic slope factor exists for Cd and trivalent Cr; there is insufficient or no data to support their oral carcinogenicity effects and as such, no value is established by the United State Environmental Protection Agency (USEPA) (ATSDR, 2018). Humans are safe if CR or TCR<1.0×10^{-4} (Janoska and Gruszecka-Kosowska, 2020).

Statistical analysis

Results of elemental composition were expressed as mean±standard deviation of three replicates. Data obtained were analyzed using one-way analysis of variance (ANOVA) with statistical package for social sciences (version 20.0 Inc., USA) to compare the elemental and anti-nutrient contents in the grains. Mean values were separated using superscript alphabets. Statistically, significant was established at *p*=0.05 using Duncan multiple range test. The relationship in the elemental and anti-nutrients composition of the grains were established using Pearson correlation coefficient and significant synergistic and antagonistic correlation were established at $p<0.05$.

Results

Levels of elements, phytate, and oxalate of the grains

The results of proportion of elements in the cereals consumed in Nigeria are shown in Table 1. The levels of essential minerals (Ca, K, Na, Mg, and P) and trace elements (Zn, Fe, Cu, Mn, Se, and Ni) in the samples were generally high. Results of potentially toxic elements (Cr, Pb, Cd, and As) revealed that the samples contain low levels of these elements. Generally, the results revealed that the barley, maize, millet, rice, sorghum, and wheat are rich in minerals and essential trace elements but low in potential toxic elements. Cd was below detectable limit in barley, maize, and millet, while the levels of the other elements varied significantly ($p=0.05$) from one sample to another. Table 1 also presents the levels of phytate and oxalate in the grains. The differences in the phytate and oxalate content of the samples were significant at $p=0.05$.

Mineral interrelationship and bioavailability

Results of the mineral and molar ratios of elements and anti-nutrients of different grains consumed in Nigeria are shown in Table 2. The ratio of Ca to Na ranged from low value of 0.52 in barley to a high value of 2.79 in millet. Ca to phytate ratio followed was low in sorghum (7.65) and wheat (9.89) but was very high in maize (48.37) and millet (34.57).

Pearson correlation coefficients

The Pearson correlation coefficients (r-values) between the elements and the anti-nutrients levels in the samples are shown in ESM Table 2. There existed significant negative correlation ($p<0.05$) and significant positive correlation ($p<0.05$) among the elements, phytate, and oxalate contents of the entire samples. The significant positive correlations are suggestive of high bioavailability of the elements at the level of the anti-nutrients reported and indicative of synergistic interrelationship among the elemental contents of the samples.

MSI

Results of the elemental safety index of the different grains are shown in Table 3. The results showed that the difference (D) between the MSIstv and MSIcv were positive (indicative of non-overloading) in some cases and negative (indicative of overloading) in some other cases.

EDI

The results of the EDI of elements of the grains are presented in Table 4. The results showed that the EDI (mg/kg/day) were higher in children when compared to adults for all the cereal grains studied. The pattern and order of the EDI of elements for children and adults for all the cereal grains were:
Fe>Zn>Mn>Cu>Cr>Ni>Se>Pb>As>Cd.

HQ and HI

The results of the HQ and HI of toxic elements in the grains are shown in Table 5. Similar to EDI, the results revealed that the HQ of the elements in the entire grains were far less than one (HQ<1).

Carcinogenic health risk

Results of the CR and TCR of potentially toxic elements in the grains are shown in Table 6. The results showed that the Cr and TCR were higher in children when compared to adults for all the grains.

Discussion

The essential elements in the grains (Table 1) were generally higher than those reported by Mohammed and Ahmad (2014) in some coarse grains used as staple food in Kano, Nigeria. For instance, the levels of K ranged from 89.22 to 193.33 mg/kg, while in our study, the values ranged from 96.30 to 644.32 mg/kg. The values obtained in our study were in agreement with those reported by Abdulrahman and Omoniyi (2016) for similar grains in Abuja, Nigeria, where K was found to range from 183.33 to 416.67 mg/kg. The differences in the elemental contents may be due to different varieties and environmental growth media (Ajala et al., 2020; Obasi et al., 2020).

The potentially toxic elements revealed that the samples contain low levels of these elements, when compared to those reported for similar grains by Pirsaheb et al. (2015) in Iran, where Cd was ranged from 0.033 mg/kg (lentil) to 1.00 mg/kg (wheat). The differences could be due to several factors such as sample size, analytical techniques employed, season of the year, and agricultural soil. However, the values were comparable to those reported in rice grain from Pakistan by Mao et al. (2019). For instance, the median Pb level was found to be 0.093 mg/kg. The Pb and Cd content were lower than the maximum tolerable limit (0.2 mg/kg for Pb and 0.1 mg/kg for Cd) allowed in cereal grains (ATSDR, 2018;

European Commission, 2006). The maximum tolerable limit specified for Cd in wheat (0.2 mg/kg), polished rice (0.4 mg/kg), and 0.35 and 0.2 mg/kg, respectively specified for As for husk and polished rice (ATSDR, 2018; European Commission, 2006) were all higher than the values obtained in the present investigation. This could imply that these grains are safe and unlikely to promote their consumers with elemental induced toxicities ranging from cellular dysfunction to cell death (EFSA, 2012).

Table 1: Elemental and anti-nutrient composition (mg/kg) of different cereals consumed in Nigeria

Elements/anti-nutrients	Barley	Maize	Millet	Rice	Sorghum	Wheat
Ca	567.87±0.08 ^{b}	2900.34±0.27 ^{f}	1382.36±0.11 ^{e}	1213.81±0.03 ^{d}	404.00±0.03 ^{a}	703.98±0.02 ^{c}
K	135.21±0.01 ^{b}	644.32±0.02 ^{f}	325.20±0.05 ^{e}	275.85±0.01 ^{d}	96.30±0.01 ^{a}	163.60±0.01 ^{c}
Na	40.48±0.01 ^{c}	77.32±0.01 ^{e}	68.30±0.00 ^{d}	30.33±0.01 ^{b}	28.75±0.00 ^{a}	40.91±0.01 ^{c}
Mg	1092.29±0.23 ^{d}	1032.18±0.19 ^{b}	494.62±0.15 ^{a}	1083.21±0.02 ^{c}	1467.53±0.03 ^{f}	1100.03±0.02 ^{e}
P	447.38±0.08 ^{c}	1464.70±0.02 ^{f}	921.60±0.01 ^{e}	758.37±0.05 ^{d}	336.34±0.01 ^{a}	382.53±0.01 ^{b}
Zn	13.33±0.07 ^{a}	19.09±0.01 ^{d}	15.93±0.01 ^{b}	20.41±0.03 ^{e}	16.41±0.01 ^{b,c}	21.08±0.01 ^{e,f}
Fe	58.56 ±0.04 ^{a}	80.26±0.01 ^{d}	64.19±0.00 ^{b}	81.81±0.01 ^{e}	65.90±0.01 ^{c}	90.69±0.01 ^{f}
Cu	1.58±0.01 ^{a}	2.29±0.01 ^{c}	1.93±0.00 ^{b}	2.48±0.00 ^{d}	1.99±0.00 ^{b}	2.61±0.00 ^{e}
Mn	7.16 ±0.01 ^{d}	8.68±0.01 ^{e,f}	4.71±0.01 ^{a}	6.11±0.01 ^{c}	5.41±0.01 ^{b}	8.1±0.01 ^{e}
Se	0.35±0.00 ^{e}	0.34±0.01 ^{de}	0.13±0.00 ^{a}	0.21±0.00 ^{b}	0.25±0.01 ^{bc}	0.32±0.00 ^{d}
Cr	1.06±0.01 ^{a}	2.31±0.01 ^{d}	1.48±0.01 ^{b}	3.81±0.01 ^{e}	1.93±0.01 ^{b,c}	4.16±0.01 ^{f}
Ni	0.42±0.01 ^{e}	0.18±0.01 ^{b}	0.20±0.00 ^{b}	0.26±0.00 ^{c}	0.11±0.01 ^{a}	0.30±0.00 ^{d}
Pb	0.06±0.03 ^{a}	0.10±0.01 ^{b}	0.06±0.01 ^{a}	0.18±0.00 ^{c}	0.08±0.00 ^{a,b}	0.06±0.00 ^{a}
Cd	0.00±0.00 ^{a}	0.00±0.00 ^{a}	0.00±0.00 ^{a}	0.02±0.01 ^{b}	0.02±0.00 ^{b}	0.02±0.00 ^{b}
As	0.02±0.00 ^{a,b}	0.03±0.00 ^{b,c}	0.01±0.00 ^{a}	0.02±0.00 ^{a,b}	0.01±0.00 ^{a}	0.01±0.00 ^{a}
Phytate	768.58±0.04 ^{b}	987.26±0.13 ^{e}	658.47±0.02 ^{a}	966.77±0.01 ^{d}	869.49±0.02 ^{c}	1171.98±0.02 ^{f}
Oxalate	467.58±0.04 ^{d}	509.73±0.15 ^{f}	431.96±0.03 ^{b}	411.81±0.01 ^{a}	442.73±0.02 ^{c}	476.49±0.01 ^{e}

Results are mean±standard deviation of three replicates. Mean values followed by the same superscript alphabets, a, b, c, d, e, along the same row are not significantly different at $p<0.05$

Table 2: Results of mineral ratios and molar ratios of elements and anti-nutrients (bioavailability) of the different cereals consumed in Nigeria

Parameter	Barley	Maize	Millet	Rice	Sorghum	Wheat
Ca/Na	0.52±0.0 ^{b}	2.81±0.02 ^{e}	2.79±0.03 ^{e}	1.12±0.02 ^{d}	0.28±0.01 ^{a}	0.64±0.02 ^{b,c}
Ca/K	4.20±0.03 ^{a}	4.50±0.01 ^{e}	4.25±0.00 ^{b}	4.40±0.02 ^{d}	4.20±0.00 ^{a}	4.30±0.03 ^{c}
Ca/P	1.27±0.02 ^{a}	1.98±0.01 ^{c,d}	1.50±0.02 ^{b}	1.60±0.01 ^{b}	1.20±0.02 ^{a}	1.84±0.02 ^{c}
Na/K	0.30±0.01 ^{c}	0.12±0.01 ^{a}	0.21±0.01 ^{b}	0.11±0.01 ^{a}	0.30±0.01 ^{c}	0.25±0.01 ^{b}
Na/Mg	0.04±0.01 ^{a}	0.07±0.00 ^{b}	0.14±0.01 ^{c}	0.03±0.01 ^{a}	0.02±0.01 ^{a}	0.04±0.00 ^{a}
Zn/Cu	8.44±0.03 ^{d}	8.34±0.03 ^{c}	8.25±0.02 ^{b}	8.23±0.07 ^{a}	8.25±0.03 ^{b}	8.08±0.03 ^{a}
Fe/Cu	37.06±0.03 ^{f}	35.05±0.03 ^{e}	33.26±0.05 ^{c}	32.99±0.13 ^{b}	33.12±0.09 ^{a}	34.75±0.11 ^{d}
[K/(Ca + Mg)]	0.03±0.01 ^{a}	0.07±0.01 ^{b,c}	0.08±0.00 ^{c}	0.05±0.0 ^{a,b}	0.02±0.01 ^{a}	0.03±0.01 ^{a}
[Ca]/[phytate]	12.17±0.13 ^{c}	48.37±0.11 ^{f}	34.57±0.07 ^{e}	20.66±0.15 ^{d}	7.65±0.12 ^{a}	9.89±0.19 ^{b}
[Phytate]/[Zn]	5.80±0.02 ^{f}	5.12±0.05 ^{c}	4.09±0.03 ^{a}	4.69±0.02 ^{b}	5.25±0.03 ^{d}	5.51±0.03 ^{e}
[Ca][Phytate]/[Zn]	0.08±0.01 ^{b}	0.37±0.02 ^{d}	0.14±0.01 ^{c}	0.14±0.01 ^{c}	0.053±0.01 ^{a}	0.097±0.01 ^{b}
[Phytate]/[Fe]	1.11±0.02 ^{d}	1.04±0.02 ^{b,c}	0.87±0.02 ^{a}	1.00±0.03 ^{b}	1.12±0.02 ^{d}	1.09±0.03 ^{c}
[Oxalate]/[Ca]	0.37±0.01 ^{d}	0.08±0.01 ^{a}	0.14±0.03 ^{b}	0.15±0.05 ^{b,c}	0.50±0.02 ^{d,e}	0.76±0.02 ^{f}

Results are mean±standard deviation of three replicates. Mean values followed by the same superscript alphabets along the same row are not significantly different at $p<0.05$

Table 3: Results of elemental safety index of the different cereals consumed in Nigeria

Element	Barley		Maize		Millet		Rice		Sorghum		Wheat	
	MSIcv	D	MSIcv	D	MSIcv	D	MSIcv	D	MSIcv	D	MSIcv	D
Ca	4.73	5.27	24.17	-14.17	11.52	-1.52	10.12	-0.12	3.37	6.63	5.87	4.13
Na	0.38	4.46	0.74	4.06	0.66	4.14	0.29	4.51	0.28	4.52	0.39	4.41
Mg	27.31	-12.31	25.81	-10.81	12.37	2.63	27.08	-12.08	36.69	-21.69	27.50	-12.50
P	3.73	6.27	12.21	-2.21	7.68	2.32	6.32	3.68	2.80	7.20	3.19	6.81
Zn	28.89	4.11	42.00	-9.00	35.05	-2.05	44.90	-11.90	36.10	-3.10	46.38	-13.38
Fe	26.16	-19.46	35.85	-29.15	28.67	-21.97	36.54	-29.84	29.43	-22.73	40.51	-33.81
Cu	17.38	15.62	25.19	7.81	21.23	11.77	27.28	5.72	21.89	11.11	28.71	4.29
Mn	10.74	-3.24	13.02	-5.52	7.07	0.43	9.17	-1.67	8.12	-0.62	12.17	-4.67
Se	2.31	-1.85	2.24	-1.78	0.86	-0.40	1.39	-0.93	1.65	-1.19	2.11	-1.65

RAI=Recommended Adequate Intake; MSIstv=Mineral Safety Index Standard Table Value; cv=Calculate Value; D=Difference between MSIstv and MSIcv

Table 4: Results of the Estimated Daily Intake (EDI) (mg/kg bw/day) of elements in some Nigerian's cereals

Element	Barley		Maize		Millet		Rice		Sorghum		Wheat	
	Adults	Children	Adults	Children	Adults	Children	Adults	Children	Adults	Children	Adults	Children
Zn	9.73E-05	4.54E-04	8.00E-03	2.51E-02	7.31E-03	1.35E-02	9.65E-03	2.29E0-2	1.05E-02	4.90E-02	1.36E-02	6.35E-02
Fe	4.34E-04	2.02E-03	3.36E-02	1.06E-01	2.95E-02	5.46E-02	3.87E-02	9.20E-02	4.22E-02	1.97E-01	5.85E-02	2.73E-01
Cu	1.17E-05	5.46E-05	9.59E-04	3.01E-03	8.86E-04	1.64E-03	1.17E-03	2.79E-03	1.27E-03	5.94E-03	1.68E-03	7.86E-03
Mn	5.30E-05	2.48E-04	3.64E-03	1.14E-02	2.16E-03	4.00E-03	2.89E-03	6.87E-03	3.46E-03	1.62E-02	5.23E-03	2.44E-02
Se	2.59E-06	1.21E-05	1.42E-04	4.60E-04	5.97E-5	1.11E-04	9.92E-05	2.36E-04	1.60E-04	7.47E-04	2.07E-04	9.64E-04
Cr	7.85E-06	3.66E-05	9.68E-04	3.04E-03	6.79E-04	1.26E-03	1.80E-03	4.28E-03	1.23E-03	5.76E-03	2.68E-03	1.25E-02
Ni	3.11E-06	1.45E-05	7.54E-05	2.37E-04	9.18E-05	1.70E-04	1.23E-04	2.92E-04	7.04E-05	3.29E-04	1.94E-04	9.04E-04
Pb	4.44E-07	2.07E-06	4.19E-05	1.31E-04	2.75E-5	5.10E-05	8.51E-05	2.02E-04	5.12E-05	2.39E-04	3.87E-05	1.81E-04
Cd	0.00	0.00	0.00	0.00	0.00	0.00	9.45E-06	2.25E-05	1.28E-05	5.97E-05	1.29E-05	6.02E-05
As	1.48E-07	6.91E-07	1.26E-05	3.94E-05	4.59E-06	8.50E-06	9.45E-06	2.25E-05	6.40E-06	2.99E-05	6.45E-06	3.01E-05

Table 5: Results of the Hazard Quotient (HQ) and Hazard Index (HI) of elements in Nigerian's cereals

Element	Barley		Maize		Millet		Rice		Sorghum		Wheat	
	Adult	Children	Adult	Children	Adult	Children	Adult	Children	Adult	Children	Adult	Children
Zn	0.0003	0.0267	0.0837	0.0015	0.0244	0.0450	0.0322	0.0765	0.0350	0.1634	0.0454	0.2116
Fe	0.0006	0.0480	0.1507	0.0029	0.0421	0.0779	0.0552	0.1314	0.0602	0.2811	0.0836	0.3902
Cu	0.0003	0.0240	0.0753	0.0014	0.0221	0.0410	0.0293	0.0697	0.0318	0.1486	0.0421	0.1965
Mn	0.0004	0.0260	0.0815	0.0018	0.0154	0.0286	0.0206	0.0491	0.0247	0.1154	0.0374	0.1745
Se	0.0005	0.0285	0.0920	0.0024	0.0119	0.0221	0.0198	0.0472	0.0320	0.1493	0.0413	0.1928
Cr	0.0000	0.0006	0.0020	0.0000	0.0005	0.0008	0.0012	0.0029	0.0008	0.0038	0.0018	0.0084
Ni	0.0002	0.0038	0.0118	0.0007	0.0046	0.0085	0.0061	0.0146	0.0035	0.0164	0.0097	0.0452
Pb	0.0001	0.0120	0.0376	0.0006	0.0079	0.0146	0.0243	0.0578	0.0146	0.0683	0.0111	0.0516
Cd	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0095	0.0225	0.0128	0.0597	0.0129	0.0602
As	0.0005	0.0419	0.1315	0.0023	0.0153	0.0283	0.0315	0.0750	0.0213	0.0995	0.0215	0.1004
HI	0.0029	0.2115	0.6661	0.0136	0.1442	0.2668	0.2297	0.5467	0.2367	1.1055	0.3068	1.4314

Table 6: Results of the incremental lifetime Cancer Risk (CR) and Total Cancer Risk (TCR) of potentially toxic elements in Nigerian's cereals

CR/TCR	Barley		Maize		Millet		Rice		Sorghum		Wheat	
	Adult	Children	Adult	Children	Adult	Children	Adult	Children	Adult	Children	Adult	Children
Pb CR	3.78E-09	1.76E-08	3.56E-07	1.12E-06	2.34E-07	4.34E-07	7.23E-07	1.72E-06	4.35E-07	2.03E-06	3.29E-07	1.54E-06
As CR	2.22E-07	1.04E-06	1.89E-05	2.63E-05	6.88E-06	1.28E-05	1.42E-05	3.37E-05	9.60E-06	4.48E-05	9.68E-06	4.52E-05
TCR	2.26E-07	1.06E-06	1.93E-05	2.74E-05	7.11E-06	1.32E-05	1.49E-05	3.54E-05	1.00E-05	4.68E-05	1.00E-05	4.67E-05

The phytate contents of the samples as also shown in Table 1 were comparatively similar to 422.29 to 1,033.16 mg /kg reported for pearl millet cultivars in India (Abdelrahaman et al., 2007). High levels of phytate in diets interfere with the bioavailability of divalent and trivalent minerals such as Ca, Mg, and Fe (Abdelrahaman et al., 2007; Adeyeye et al., 2012; Ajala et al., 2020). In the same manner, high levels of oxalate in foods interfere with mineral metabolism especially divalent metals such as Ca and Mg (Abdelrahaman et al., 2007; Gemede, 2020; Gemede and Ratta, 2018). Processing such cooking, roasting, and drying among others could reduce the level of anti-nutrients such as phytate and oxalate in plant-based foodstuffs (Gemede and Ratta, 2018).

The results of ratios of elements as shown in Table 2 revealed that the most of the samples were within the range of standard values and were in variance with values reported for mineral element-rich plants foods consumed in Nigeria (Adeyeye et al., 2012). The ratios of Ca/P in this study differ from 0.546 to 0.997 obtained for fast foods. The difference could be attributed to the nutrients lost during processing. The Ca/phytate molar ratios in the entire samples were greater than the critical minimum value of 6 required for efficient absorption of Ca from food crops (Lopez et al., 2002); thus, Ca would be readily bioavailable for uptake from these grains.

Phytate/Zn molar ratio revealed that Zn will be highly bioavailable from millet and rice and moderately bioavailable from barley, maize, sorghum, and wheat with respect to the recommended values (Hailu and Addis, 2016). The [Ca][phytate]/[Zn] molar ratio is far lower than 0.5 mol/kg critical maximum limit set for Ca interference (Lopez et al., 2002). Thus Zn from these grains would be readily bioavailable for maximum absorption. The phytate/Fe molar ratios for millet and rice were less than one (<1), indicative of good iron bioavailability and slightly greater than one (>1) for barley, maize, sorghum, and wheat predictive of poor iron bioavailability (Lopez et al., 2002). Oxalate/Ca molar ratios were below the maximum critical set limit of 2.5 (Abdelrahaman et al., 2007) and as such, predictive that these samples are good sources of Ca for animals and humans.

In Table 3, the differences in the safety index were positive for Na and Cu, and negative for Fe and Se, which implies significant overloading of Fe and Se in the entire grains. Dangers associated with Fe and Se overload include but not limited to haemorrhagic necrosis and selenosis, respectively. However, it is important to note that other complex metabolic factors determine mineral overloading at cellular levels (Institute of Medicine, 2001; McDowell, 2003).

The results on Table 4 showed that the EDI of Zn, Fe, Cu, Mn, Se, Pb, Cd, and As for adults and children were lower than the Recommended Dietary Allowances (RDA) set by standard agencies (EFSA, 2012; European Commission, 2006). No average requirement and population RI was defined for Cr and Ni (EFSA, 2014). Adequate reference intakes for Se and Mn (EFSA, 2014) were above the values obtained in this study. The low level of EDI of these elements in all the cereal grains implies low or no potential health risk for their consumers. Similar results of 0.0003, 0.193, 0.075, 3.94; and 3.16 mg/kg bw/day, for As, Cd, Cu, Ni, and Pb, respectively are reported for different cereal grains cultivated on agricultural soils in Poland (Gruszecka-Kosowska, 2020). However, values reported in this study were lower than values reported by Huang et al. (2013). They reported EDI of As, Cd, and Pb to be 1.02, 0.64, and 1.26 mg/kg bw/day for adults, and 0.63, 0.83, and 1.63 mg/kg bw/day for children, respectively in rice consumed by the population of Zhejiang, China.

The HQ and HI of the elements were higher in children compared to adults with Fe and Cr having the highest and least value, respectively. This is an indication that children are more vulnerable to toxic chemicals than adults due to greater exposures to toxic chemicals for their body weight than adults (Landrigan and Goldman, 2011). Also, the metabolic pathways of children are immature and may not effectively metabolize toxic chemicals which rapidly disrupt their developmental processes (Landrigan and Goldman, 2011). The results indicated no health risk for Cd in barley, maize, and millet for both adults and children. Similar results are reported for cereal grains from other countries (Antoniadis et al., 2019; Gruszecka-Kosowska, 2020; Huang et al., 2013). The implication of these results is that elemental induced non-carcinogenic toxicity effects such as neurotoxicity, nephrotoxicity, hepatotoxicity, and anaemia among others associated with excessive intake; and absorption of these elements will not arise from consumption of these cereal grains (EFSA, 2012, 2014).

Although, the HI value was greater than one (HI>1) for children in wheat and sorghum, children that consume them may not experience elemental induced toxicity because cellular interrelationship among these elements may produce antagonist effects in their mechanism of action; absorption of one may impair the absorption of the other (Institute of Medicine, 2001). HI less than one (HI<1) for children in barley, maize, millet, and rice and for adults in all the cereal grains is an indication that their target consumers will experience no potential health effects from the elements studied. These are in line with reported values for cereal grains from other countries (Gruszecka-Kosowska, 2020; Satpathy et al., 2014) which had HI<1 and were therefore within safe limits.

The CR and TCR values of the elements in the cereals obtained for children when compared to adult may be attributed to high absorption rate of toxic elements by children for their body weight compared to adults (Landrigan and Goldman, 2011). Though, As was the major contributor to TCR, its CR, and TCR values and that of Pb were below the maximum threshold safe limit ($CR<1.0\times10^{-4}$); hence no potential risk of incremental lifetime Pb- or As-induced carcinogenicity. Similar results for cereal grains from other countries are reported (Antoniadis et al., 2019; Gruszecka-Kosowska, 2020).

Pb exposure through diet is linked to development of renal cell carcinoma and malignant growth in brain, larynx, and bladder tissues (Silbergeld et al., 2000) while As dietary exposure causes a number of malignant cell growths leading to lung, bladder, and skin cancer in humans (Martinez et al., 2011). Available evidence showed that Cr (III), the natural dietary form of Cr in foods is not carcinogenic in experimental animals (EFSA, 2014). Evidence of carcinogenic effects of dietary intake of Cd are conflicting (Adams et al., 2014). At present, because of the above uncertainty, oral carcinogenicity slope factors have not been assigned to Cr (III) and Cd (ATSDR, 2018). This study revealed that there is no CR in the consumption of these grains from single or combined effects of Pb and/or As.

Conclusion

This study revealed that barley, maize, millet, rice, sorghum, and wheat available in Nigeria markets contain varying quantities of essential elements, potentially toxic elements, and antinutrients (phytate and oxalate). The essential elements present in grains were highly bioavailable *in vitro* despite the presence of phytate and oxalate. The levels of Se and Fe overload in all the cereals were not significant to cause any toxicological health risk since their HQ values were at an acceptable risk level. HI values for children in wheat and sorghum exceeded USEPA threshold limit; hence, their utilization in complementary feeding calls for serious concern over children's health. Although, the CR values for all the grains were at acceptable risk levels for adults and children, nevertheless, the CR may be higher, if other carcinogens are taken into play. Therefore, there is a need for regular and routine assessment of toxic elements in the grains to ensure their wholesomeness and safety of the consumers.

Author contributions

N.A.O. designed the study and wrote the protocol; S.E.O. performed the sampling and managed the analyses of the study; L.O.A. collected samples, involved in the laboratory analysis, and reviewed the manuscript; G.O.A. conceptualized, supervised, and involved in the laboratory analysis; C.A. conceptualized, drafted, and reviewed the manuscript; S.S.O. Visualized and performed statistical analysis; G.N.O. collected samples from fields and involved in the laboratory analysis. All authors read and approved the final manuscript.

Conflicts of interest

The authors declare that there was no potential conflict of interest.

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