Assessment of heavy metals concentration in selected foods sold in markets within Port-Harcourt city, Nigeria

Abstract

Heavy metals are toxic environmental substances which may bioaccumulate up a food chain and pose threat to the health of humans. The present study investigated the concentrations of heavy metals (Zn, Fe, Cu, Pb, Cd) in selected foods (wheat, millet, millet pap, maize, maize pap, groundnut, kuli-kuli and ose-oji) purchased from different markets in Port Harcourt, Nigeria using Atomic Absorption spectrophotometry (AAS). The results indicate that the concentration of the heavy metals (mg/Kg) varied across the various samples: Zn (4.68±0.07-45.73±0.04), Fe (n.d-145.19±0.17), Cu (4.54±0.05-9.55±0.03), Pb (3.96±0.04-15.68±0.08), Cd (0.0156±0.01-0.2688±0.05). With the exception of Cd and Pb, other heavy metals studied were within acceptable limits. The levels of heavy metals in the pap samples (millet and maize pap) were of concern because these are popular weaning foods in Nigeria hence these metals could pose threat to the health of infants. Kuli-Kuli and ose-oji are also samples of interest because of their wide consumption and elevated levels of metals (Zn and Pb). There should be adequate monitoring of heavy metal content of these food sources to prevent incidence of heavy metal toxicity which may result from bioaccumulation with continued consumption of these food by the public.

Keywords: heavy metals, bioaccumulation, health, toxicity, density, samples, biomolecules, pollution, groundnut, wheat, millet, maize, heart, kidney, lungs, immune system

Introduction

Heavy metals are metallic elements which have a high atomic weight and a density much greater (at least 5 times) than that of water and is harmful to most organisms even when present at low concentration. Toxic heavy metals comprise a group of minerals that have no known function in the body and are harmful to humans. Heavy metals exist in natural and contaminated environments and cannot be easily detoxified via degradation, resulting in their persistence in the environment. Many of these metals, such as Cd, Pb and Cr, are carcinogens and are involved in several diseases, including Alzheimer’s, Parkinson’s, multiple sclerosis, osteoporosis, developmental disorders and failure of several organs (e.g., heart, kidney, lungs, immune system). However, some of these metals, such as Ni, Cu and Zn, are essential minerals that are needed for a variety of biomolecules to maintain the normal structure, function and proliferation of cells. Rapid and unorganised urban and industrial developments have contributed to the elevated levels of heavy metals in the urban environment of developing countries including Nigeria. In the Niger Delta region, due to the level of pollution as a result of oil exploration activities, there has been an increased level of toxic metals in air, water and agricultural soils with a resultant increased uptake and deposition on foods (including processed foods) such as cereals, rice and vegetables thus posing serious health implications to the health of consumers. Different studies have shown varying amounts of heavy metals in various food sources in Nigeria. Some metals are naturally found in the body and are essential to human health such as Iron which prevents anemia, zinc is an essential cofactor in several enzymes of biochemical importance, magnesium and copper also serve other important metabolic functions. Heavy metals are not metabolized by the body of organisms (aquatic and terrestrial) hence they bio-accumulate. If heavy metals enter and accumulate in body tissues faster than the body’s detoxification process can handle, a gradual build-up of these toxins will occur. From the foregoing, it is evident that effective assessment of food is necessary to ensure best practices and consumer protection. Wheat, millet, maize, groundnut and their respective derivatives (millet pap, maize pap, kuli-kuli and ose-oji) are widely consumed staple foods in Nigeria. However, the fine details about their safety have yet to be completely studied. Hence, this study aims to assess the levels of some heavy metals in wheat, millet, maize, groundnut and their respective derivatives marketed within Port Harcourt, Rivers State, Nigeria.

Materials

Wheat, millet, millet pap, maize, maize pap, groundnut (raw), kuli-kuli, and ose-oji samples were collected from three markets (Mile One market, Oil Mill market and Creek Road market) located within Port Harcourt metropolis. These markets are the mostly patronised markets in the metropolis, thus the samples serve as a representation of the study area. The grains were purchased from market stalls and a composite mixture made to obtain an even mix of grains from different shops within each market. The kuli-kuli, ose-oji and pap samples were randomly purchased from vendors in the three markets of Mile One market, Oil Mill market and Creek Road market, respectively.

Sample preparation

Kuli-kuli samples are prepared from groundnut. The groundnuts are fried and dehusked. It is then ground to paste and moulded to desired form, then dried. Seasoning cubes and pepper can be optionally added.
Ose-oji is prepared similarly from groundnut. Measured quantities of ingredients such as groundnut, crayfish, chili pepper and salt are ground together. Millet and maize pap are prepared by soaking the grain in water for 2-3 days (changing the water regularly); it is then washed and ground, and sieved with a muslin bag and allowed to settle down. It is then prepared into gruel by dissolving in cold water and adding hot water and turning rapidly until it thickens.

Methods

The assessment of heavy metals was performed using the method described by.3 The samples were oven dried at 105 °C to constant weight for 2 hours, cooled to room temperature and ground to fine powder using Kenwood electric miller and exactly 1 g of the ground sample was quantitatively transferred into a well-glazed porcelain crucible, placed in a muffle furnace and ashed at 450 °C for 12 hours. The resultant ash was cooled to room temperature and digested to a clear solution with 5 ml of 5M HNO₃. The residue was then filtered into a calibrated 50 ml volumetric flask using Whatman No. 41 filter paper, and the solution was made up to mark with deionised water. The total concentrations of the metals in the digests were determined by aspirating the solution into Buck Model 210A atomic absorption spectrophotometer after the necessary standardization procedures.

Results

The heavy metal assessment of the samples studied reveal that wheat and millet grains have non-significant concentrations of zinc Table 1 ranging between 28.53±0.05 to 43.39±0.13 mg/kg in the three sampling sites (mile one, creek road and oil mill markets). However, the concentration (mg/kg) of zinc in millet pap (13.69±0.05) from creek road market is significantly higher (p<0.05) when compared to mile one (9.61±0.07) and oil mill (11.69±0.02) markets, respectively. Similarly, millet grains from creek road market has zinc concentration (25.44±0.17 mg/kg) that is significant (p<0.05) from oil mill pap (28.46±0.07 mg/kg) and mile one (26.47±0.04 mg/kg) markets. The level of zinc in maize pap ranged between 7.17±0.03 to 9.16±0.03 mg/kg in the three markets. The concentration of zinc in raw groundnut, Kuli-kuli and ose-oji in creek road market showed significant difference (p<0.05) from both oil and mile one markets, respectively. From the results in Table 2, the concentration of iron in the samples ranged from 30.26±0.22 to 145.19±0.17 mg/kg in the three sampling sites (Mile one, Creek road and Oil mill markets). Iron concentration in wheat samples from Oil mill market (80.47±0.06 mg/kg) was significantly lower (p<0.05) when compared with the samples from Mile One market (90.77±0.08 mg/kg) and Creek road market (85.23±0.20 mg/kg) respectively. No significant difference was seen in the millet grains from the three markets; a range of 30.26±0.22 to 35.34±0.19 mg/kg. Kuli-kuli from Mile One market had significantly lower (p<0.05) concentration of iron (142.22±0.11 mg/kg) when compared with Oil mill market (145.19±0.17 mg/kg) and Creek road market (144.18±0.09) respectively. Iron was not detected in maize grains, groundnut, maize pap, millet pap and Ose-Oji from the three markets of sampling.

The concentration of copper Table 3 indicates a range from 5.16±0.05 to 9.55±0.03 mg/kg across the various samples and three markets. The concentration of copper in wheat grains from Mile One market (5.55±0.04 mg/kg) was significantly lower than Creek road (9.55±0.03 mg/kg) and Oil mill (8.59±0.03 mg/kg). Similarly, wheat grains from Mile One market had significantly lower copper concentration (5.37±0.02 mg/kg) when compared with Creek road (8.55±0.05 mg/kg) and Oil mill (7.43±0.02 mg/kg) respectively. No significant difference (p<0.05) was seen in the maize grains from the three markets; a range of 5.19±0.24 to 6.05±0.04 mg/kg was however observed. Groundnut from Oil mill market had significantly higher (p<0.05) copper concentration (6.87±0.03 mg/kg) when compared with Mile One and Creek road markets (5.05±0.49 and 4.89±0.03 mg/kg respectively). No significant difference was seen amongst the millet pap samples however a range of 5.31±0.19 to 5.44±0.03 mg/kg was observed. A similar trend was observed in millet pap samples where Oil mill had the highest concentration (5.59±0.01 mg/kg) while Creek road had the lowest value of 4.59±0.01 mg/kg. No significant difference was observed amongst Kuli-kuli with the highest values being 7.49±0.01 mg/kg (Oil mill) and lowest value of 6.36±0.20 mg/kg (Creek road market). Similarly, no significant difference (p<0.05) was seen in the Ose-Oji samples; a range of 4.54±0.05 to 5.66±0.22 mg/kg was observed.

Table 1 Level of zinc (mg/Kg) in selected foods

| Sample            | Markets          | Value  |
|-------------------|------------------|--------|
| Wheat grains      | Mile One         | 29.49±0.06a |
|                   | Creek Road       | 28.53±0.05a |
|                   | Oil Mill         | 31.28±0.02a |
| Millet grains      | Mile One         | 38.24±0.06a |
|                   | Creek Road       | 43.39±0.13a |
|                   | Oil Mill         | 42.41±0.20a |
| Maize grains       | Mile One         | 26.47±0.04a |
|                   | Creek Road       | 24.54±0.17b |
|                   | Oil Mill         | 28.46±0.07a |
| Groundnut (raw)    | Mile One         | 4.68±0.07a  |
|                   | Creek Road       | 7.68±0.17b  |
|                   | Oil Mill         | 8.65±0.12b  |
| Millet pap (raw)   | Mile One         | 9.61±0.07a  |
|                   | Creek Road       | 13.69±0.05b |
|                   | Oil Mill         | 11.69±0.02c |
| Maize pap (raw)    | Mile One         | 7.17±0.03a  |
|                   | Creek Road       | 6.16±0.01a  |
|                   | Oil Mill         | 9.16±0.03a  |
| Kuli-kuli          | Mile One         | 45.73±0.04a |
|                   | Creek Road       | 43.81±0.14b |
|                   | Oil Mill         | 41.65±0.14c |
| Ose-oji            | Mile One         | 20.28±0.01a |
|                   | Creek Road       | 22.27±0.02b |
|                   | Oil Mill         | 18.26±0.01c |

Table 2 Level of iron (mg/Kg) in selected foods

| Sample            | Markets          | Value  |
|-------------------|------------------|--------|
| Wheat grains      | Mile ONE         | 90.77±0.08a |
|                   | Creek Road       | 85.23±0.20a |
|                   | Oil Mill         | 80.47±0.06b |
| Millet grains      | Mile One         | 32.07±0.05a |
|                   | Creek Road       | 35.34±0.19a |
|                   | Oil Mill         | 30.26±0.22a |
| Maize grains       | Mile One         | ND     |
|                   | Creek Road       | ND     |
|                   | Oil Mill         | ND     |
| Groundnut (raw)    | Mile One         | ND     |
|                   | Creek Road       | ND     |
|                   | Oil Mill         | ND     |
| Millet Pap (raw)   | Mile One         | ND     |
|                   | Creek Road       | ND     |
|                   | Oil Mill         | ND     |
| Maize pap (raw)    | Mile One         | ND     |
|                   | Creek Road       | ND     |
|                   | Oil Mill         | ND     |
| Kuli-kuli          | Mile One         | 142.22±0.11a |
|                   | Creek Road       | 144.18±0.09b |
|                   | Oil Mill         | 145.19±0.17b |
| Ose-Oji            | Mile One         | ND     |
|                   | Creek Road       | ND     |
|                   | Oil Mill         | ND     |

Values are presented as mean ± S.D of triplicate determination
Values with different superscript alphabets on the same row are significantly different (p<0.05)

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The concentration of lead in the studied samples (Table 4) shows a range of 3.96±0.04 to 15.68±0.08mg/kg. Wheat grains from Oil mill market had a significantly lower (p<0.05) lead concentration (3.96±0.04mg/kg) when compared with Mile One (4.96±0.13mg/kg) and Creek road (5.61±0.26mg/kg) markets. The concentration of lead in millet grains was highest in Mile one market (10.43±0.31mg/kg) and lowest in Oil mill market (5.64±0.17mg/kg); when compared, there was a significant difference (p<0.05) amongst all three markets. No significant difference was observed in the millet grains across the three markets, the highest being 9.12±0.07 (Creek road) and lowest was 8.72±0.26mg/kg. Lead concentration in groundnut samples from Creek road market was significantly higher (p<0.05) when compared with Mile One (9.62±0.40mg/kg) and Oil mill market (8.35±0.18mg/kg) respectively. Millet pap sample from Mile one market has significantly higher lead concentration (15.68±0.08mg/kg) when compared with Creek road market (11.52±0.36mg/kg) and Oil mill market (13.76±0.06mg/kg). Millet pap sample from Mile one had the highest concentration of lead (11.46±0.26mg/kg) and was significantly higher than Creek road (9.75±0.08mg/kg) and Oil mill market (9.78±0.02mg/kg). Kuli-kuli from Mile one market had the highest lead concentration of 11.46±0.26mg/kg and was significantly higher than Creek road (9.75±0.08mg/kg) and Oil mill (7.68±0.02mg/kg) respectively. Kuli-kuli from Mile one market had the highest lead concentration of 11.64±0.08mg/kg and was significantly higher than Creek road (7.83±0.05mg/kg) and Oil mill (6.56±0.13mg/kg) markets respectively. There was no significant difference in the Ose-Oji samples from the three sampling sites; a range of 7.84±0.20 to 8.67±0.23mg/kg was observed. There was no significant difference in the concentration of cadmium in the various samples and sampling locations (Table 5). The highest concentration of cadmium was seen in Kuli-kuli from Creek road market (0.268±0.05 mg/kg) while the lowest was seen in groundnut samples from Oil mill market (0.015±0.01mg/kg). The average concentration of toxic metals in all the samples analyzed showed the following trend: Fe<Zn>Pb<Cu>Cd.

### Table 3 Level of copper (mg/Kg) in selected foods

| Sample              | Markets         | Mile One | Creek Road | Oil Mill |
|---------------------|-----------------|----------|------------|----------|
| Wheat grains        |                 | 5.55±0.04 a | 9.55±0.03b | 8.59±0.03b |
| Millet grains       |                 | 5.37±0.02a | 8.55±0.05b | 7.43±0.02b |
| Maize grains        |                 | 5.19±0.24a | 5.06±0.03a | 6.05±0.04a |
| Groundnut (raw)     |                 | 5.05±0.49a | 4.89±0.03a | 6.87±0.03b |
| Millet Pap (raw)    |                 | 5.44±0.03a | 5.31±0.19a | 5.42±0.09a |
| Maize pap (raw)     |                 | 5.21±0.48a | 4.59±0.01a | 5.59±0.01a |
| Kuli-kuli           |                 | 6.47±0.35a | 6.36±0.20a | 7.49±0.001a |
| Ose-Oji             |                 | 5.16±0.05a | 5.66±0.22a | 5.45±0.05a |

Values are presented as mean ± 5.D of triplicate determination.

### Table 4 Level of lead (mg/Kg) in selected foods

| Sample              | Markets         | Mile One | Creek Road | Oil Mill |
|---------------------|-----------------|----------|------------|----------|
| Wheat grains        |                 | 4.96±0.13a | 5.61±0.26a | 3.96±0.04b |
| Millet grains       |                 | 10.43±0.31a | 7.86±0.28b | 5.64±0.17c |

Values with different superscript alphabets on the same row are significantly different (p<0.05).

### Table 6 Regulatory limits of metals in foods

| Metals | WHO/FAO | NAFDAC | EC/CODEX |
|--------|---------|--------|----------|
| Cd     | 1       | -      | 0.2      |
| Cu     | 30      | 20     | 0.3      |
| Pb     | 2       | 2      | 0.3      |
| Zn     | 60      | 50     | <50      |
| Fe     | 48      | -      | -        |

Source: Edward, et al.,6

**Discussion**

The need to effectively and efficiently evaluate the safety of processed and unprocessed food cannot be overemphasized as the safety of consumers’ needs to be protected. According to the National Bureau of Statistics,1 a staggering 112 million of the Nigerian population live below $1 per day, thus majority of the populace depend on ready-made snacks and cheap food sold in major markets while overlooking safety concerns. Also, grains such as millet, wheat and maize are major export produce for Nigeria as countries in the Sahel, such as Niger, Chad, Burkina Faso, and Mali continue to rely on Nigeria’s grain with an estimated annual export of 400,000 tonnes per annum.10 Thus, the current study assessed the occurrence of some heavy metals in some selected grain and grain-derived products. Food materials offered for sale within cities are exposed to a wide array of toxic metals from various sources. There is an increasing concern on environmental pollution which has a very significant contribution to food pollution. The average consumer is unaware of the likely dangers of these substances in the food they consume hence adequate and routine check is needed to ensure consumer safety. The findings of this study indicate that there was no significant difference in the concentration of zinc amongst the wheat samples, millet samples and maize pap samples; other samples showed significant differences (p<0.05) between the three different markets. Various researchers have shown that heavy metals in different food sources in Nigeria and the findings of this work corroborate various findings of previous studies.1 reported high levels of Pb in Kuli-kuli samples marketed in Abeokuta, South-West, Nigeria11 reported heavy metals levels within permissible limits in cereals (wheat, barley, sorghum and maize) collected from local markets in Ambo city, Ethiopia1 reported elevated levels of heavy metals in maize grown in industrial areas of Ogun state, South-Western Nigeria reported that there was elevated levels.
of heavy metals in vegetables, cereals and fruits in Saudi Arabian markets (Table 6). The findings of this study corroborate the above reports and also show that ose-oji contains high levels of certain heavy metals (Zn and Pb) and hence must be carefully monitored.

Conclusion
Toxic metals bioaccumulation is a threat to the health of consumers; the food samples studied (wheat, millet, maize, maize pap, millet pap, groundnut, kali-kuli and ose-oji) are popular staple foods with a high consumption rates hence, to ensure the safety of consumers, it is therefore recommended that foods sold in the open market should be regularly screened and monitored to reduce any incidence of toxic metal build up and heavy metals related effects in the body of consumers. Lead is a carcinogenic toxic metal whose levels were detected above WHO permissible limits. Regulatory agencies should carefully monitor the heavy metals levels of food in circulation from time to time to ascertain and control incidence of heavy metal toxicity.

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Conflict of interest
The author declares there is no conflict of interest.

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