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INVESTIGATION OF HEAVY METAL CONTAMINATION IN BREAD BAKED AND SOLD IN MAKURDI METROPOLIS, BENUE STATE NIGERIA

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Abstract

Heavy metals are pollutants that are of global significance due to their toxicological properties when their intake significantly exceeds recommended levels. They are persistent in the environment, and may be unintentionally present in raw materials used for production of bread; they may migrate from packaging into food, or find their way into finished food products due to anthropogenic activities. The present study investigated the presence of heavy metals in bread baked and sold in Makurdi, Metropolis, to ascertain their safety for consumption. Twenty different bread brands were sampled twice from bakeries and distribution outlets within Makurdi, metropolis respectively. The heavy metal analysis was carried out using Atomic Absorption Spectrophotometer (AAS). The varied concentrations of heavy metals in mg/kg of Fe, Pb, Cr, Zn, Ni, and Cd in Bread Loaves from Bakeries (BFB) and in Bread Loaves from Distribution Outlets (BFD) were determined. Cd was not detected in BFB and flour, but it was present in one sample in BFD. Duncan Multiple Range Test (DMRT) was employed to separate the means. Though, most of the studied heavy metals were within permissible limits, caution should be taken when consuming bread, because of their ability to persist and bio-accumulate in bio-systems.

Keywords: Bread, Heavy metals, Baking, Makurdi

INTRODUCTION

Heavy metals are elements that form positive ions in solution and have a density five times greater than that of water (Duffus, 2003). They are beneficial in minute quantities with the exception of Lead (Pb), Cadmium (Cd) and Mercury (Hg) are toxic even in very low concentrations (Sabry, 2014), but prolonged ingestion of, and exposure to excess quantities becomes toxic to human health (Jonathan *et al.,* 2009). They are significant in nutrition, either for their essential nature or their toxicological properties (Khaniki, 2005). Their harmful effects on the body could be neurotoxic, nephrotoxic, fetotoxic, teratogenic, or even carcinogenic when their intake significantly exceed the recommended levels. Also, they are not only toxic to living tissues, but have degrading effects on the environments- they are able to remain persistent in the environment once discharged. Furthermore, trace metals have long half-life of about a year when they get absorbed in body tissues and organs (Gholam *et al.,* 2005; Bando *et al.*, 2023).

Globally, substantial amounts of trace metals are annually added to the environment via pollution arising from natural and anthropogenic activities/processes. These have resulted in the contamination of soil, atmosphere, underground and surface water, and food. Thus, trace metals bio-accumulate and bio-magnify as they find their ways into human and animal tissues through the food chain, and food becomes the ultimate source of metal intake into the human body (Khalid and Rehman, 2013).

Bread is a staple that provides about 50 – 90 % of calories and protein intake (Agu *et al.,* 2011). In addition to carbohydrates, proteins, and some vitamins, bread is also an important source of minerals and trace metals. It is prepared by baking dough which consists of several ingredients. The principal ingredients are flour, yeast, salt and water;

optional ingredients include fat, sugar, milk and some additives (oxidants, emulsifying agents and preservatives) (Wei and Yang, 2010; Bando *et al*., 2023). Also, bread dates back to the Neolithic era and it is one of the most consumed flour products in most societies around the world. Statistics from a survey conducted on bread consumption in Nigeria in 2004, showed that bread is one of the most consumed foods in homes, restaurants and hotels, with predominant consumption among the poor and young ones who constitute more than 70% of the over 150 million people in the country (Wei and Yang, 2010).

Keeping in sight the large scale production and consumption of bread, it is paramount to assess the presence and levels of trace metals in bread and compare with recognized standards (permissible limits), in other to ascertain its safety. Furthermore, the determination of the levels of trace metals in bread has made an important contribution to environmental sciences and toxicology (Khalid and Rehman, 2013; Bando *et al*., 2019). This is because it informs us about environmental contaminants which are naturally not part of the food chain. It further suggests the medium via which these contaminants find their way into the food chain; either via our anthropogenic processes such as processing, packaging, storing, distribution, and/or through heavy metal uptakes by crop plants. This study aimed at investigating heavy metal contamination in frequently consumed bread baked within Makurdi metropolis, Benue State.

METHODS

Study Area

The study was carried out within Makurdi Metropolis (Figure 1), the administrative capital of Benue State, Nigeria. The city is located in central Nigeria along the Benue River. Its geographical coordinates are 7.44°N and 8.32°E, with a population of over 500,000 people **(**The World Gazetteer, 2007**)**.

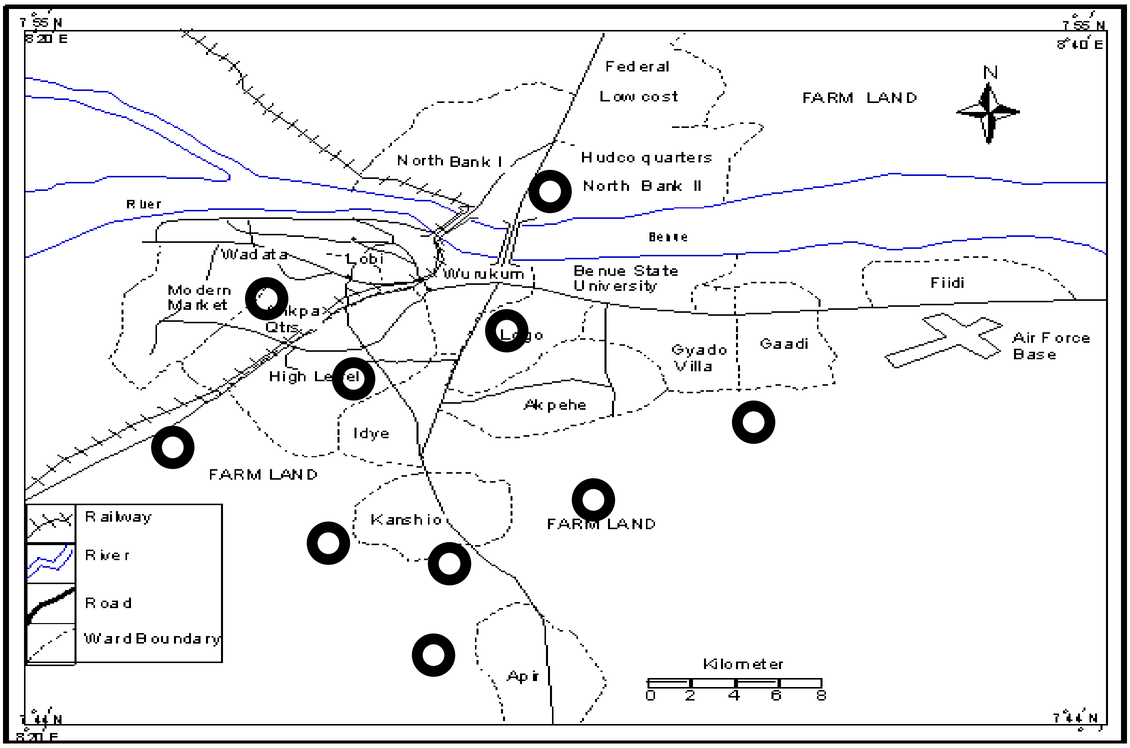

Figure 1: Map Showing Sampling Site – Makurdi, Benue State, Nigeria.

Source: - **www.maplandia.com/nigeria/benue**

Research Design

The work adopted both survey and experimental design. A structured questionnaire was designed and distributed in a simple random fashion to people living in the study area. 500 copies of the questionnaire were distributed to respondents residing in North-bank, Wurukum, High-level, Wadata, Modern market, Gboko road, New GRA, Old GRA, Abu King Shulluwa Road and Kanshio respectively. The questionnaire was divided into two sections, A and B (section A contained demographic information of the respondents, while section B generated information on the respondent's choice of bread). The data generated were used to determine the frequently consumed bread by respondents in Makurdi. The experimental method was based on the laboratory analyses of bread samples obtained from bakeries and distribution outlets in the study area.

Sample collection

Twenty samples of frequently consumed bread brands baked in Makurdi were obtained twice each from bakeries and distribution outlets in North-bank, Wurukum, High-level, Wadata, Modern market, Gboko road, New GRA, GRA, Abu King Shulluwa Road and Kanshio respectively.

Sample Preparation

The bread samples were sliced and allowed to air dry at room temperature and then oven dried at 60ºC (Khaniki *et al.,* 2005; Khalid and Rehman, 2013). The dried samples were each ground to fine powder in an agate mortar and thoroughly mixed to homogeneity, the mortar was rinsed after each sample pounding to avoid cross contamination. The ground samples were sieved using sethi standard test sieve BBS 40 and stored in sterile, air tight sample bottles with screw caps, then labelled accordingly.

Analysis of Heavy Metals

Sample Digestion

The samples digestion was done in Chemistry Department Laboratory at University of Benin, Edo State. The protocol went thus; 1.0g of the powdered bread sample was weighed using an electric weighing balance (model AR2130 Ohaus Corporation China) and then put into flat bottom flask. 10ml of $HCl/HClO_4$ was measured using a measuring cylinder in ratio 2:1, and added to the weighed sample in the flat bottom flask, and shaken. The flask was then heated on a hot plate in a fume hood, until a transparent solution was obtained. The transparent solution was then filtered with a filter paper (Whatman No. 1) into a cylindrical flask to remove residual impurities. The filtrate was then diluted with deionised water to a mark of 100 ml. It was then transferred into a sample bottle for analysis of heavy metals. Similar procedure was used to prepare sample blanks, and transferred into a sample bottle for analysis.

Detection of Heavy Metals

An Atomic Absorption Spectrophotometer (Buck Scientific Model – 210 VGP and Buck Scientific, USA) was used to analyse all the digested samples. The spectrophotometer was calibrated by analysing three standard and blank solutions, before the commencement of analyses for the selected metals. The official method of analysis according to the Association of Official Analytical Chemists (AOAC, 1990) was followed. The heavy metals analysed were Lead, Cadmium, Chromium, Nickel, Iron, and Zinc. The samples were analysed in triplicates for quality assurance.

Statistical Analyses

Descriptive statistics was used to analyse the data generated from the questionnaires. Data generated from analysed samples were subjected to ANOVA using Statistical Package for Social Scientists (SPSS, version 21.0) to test for statistical significance set at $P < 0.05$.

RESULTS

Tables (1 to 3) revealed the concentration of the heavy metals in bread samples collected from bakeries and distribution outlets, and flour samples.

Table 1: Mean Concentration of Heavy Metals (mg/kg) in Samples from Distribution Outlets

Samples	Concentration of Heavy Metals (mg/kg)*					
	Fe	Pb	Cr	Zn	Ni	Cd
A	1.335±0.021^{j}	0.425±0.007^{f}	0.835±0.191^{fgh}	0.455±0.021^{cde}	0.005±0.007^{a}	ND
B	0.880±0.014^{g}	0.440±0.014^{f}	0.730±0.0424^{defgh}	0.360±0.057^{abcd}	0.095±0.007^{cde}	ND
C	0.685±0.0212^{e}	0.23±0.000^{bc}	0.295±0.035^{abc}	0.390±0.057^{abcde}	0.100±0.000^{de}	0.025±0.005^{b}
D	1.480±0.028^{l}	0.41±0.000^{f}	0.085±0.035^{a}	0.510±0.099^{e}	0.115±0.007^{e}	ND
E	0.760±0.000^{f}	0.66±0.014^{g}	0.650±0.000^{cdefg}	0.410±0.014^{abcde}	ND	ND
F	0.665±0.007^{e}	0.415±0.021^{f}	1.075±0.035^{hi}	0.415±0.021^{bcde}	0.110±0.014^{e}	ND
G	0.775±0.021^{f}	0.355±0.007^{e}	0.365±0.035^{abcd}	0.375±0.35^{abcd}	0.105±0.007^{e}	ND
H	1.225±0.021^{i}	0.420±0.014^{f}	0.360±0.014^{abcd}	0.475±0.050^{cde}	0.015±0.021^{a}	ND
I	0.370±0.000^{b}	0.34±0.042^{e}	0.385±0.021^{abcd}	0.385±0.021^{abcde}	0.115±0.021^{e}	ND
J	0.475±0.035^{d}	0.340±0.028^{e}	0.495±0.021^{bcdef}	0.41±0.057^{abcde}	0.100±0.000^{de}	ND
K	0.315±0.021a	0.360±0.014^{e}	0.360±0.000^{abcd}	0.400±0.014^{abcde}	0.100±0.000^{de}	ND
L	1.390±0.000^{k}	0.415±0.021^{f}	1.200±0.000^{i}	0.435±0.050^{cde}	0.065±0.018^{abcde}	ND
M	0.740±0.000^{f}	0.450±0.000^{f}	0.980±0.014^{ghi}	0.470±0.042^{cde}	0.080 ±0.011^{bcde}	ND
N	1.215±0.021^{i}	0.345±0.021^{e}	0.665±0.021^{cdefg}	0.430±0.071^{bcde}	0.005±0.07^{a}	ND
O	0.880±0.014^{g}	0.010±0.000^{a}	0.750±0.014^{efgh}	0.400 ±0.028^{abcde}	0.035±0.015^{abcd}	ND
P	0.870±0.000^{g}	0.415±0.021^{f}	0.130±0.014^{ab}	0.470±0.042^{cde}	0.095±0.007^{cde}	ND
Q	0.500±0.014^{d}	0.255±0.021^{c}	0.125±0.007^{ab}	0.280±0.042^{a}	0.090±0.014^{cde}	ND
R	0.650±0.000^{e}	0.295±0.007^{d}	0.175±0.035^{ab}	0.300±0.071^{ab}	0.030±0.028^{abc}	ND
S	1.125±0.007^{h}	0.200±0.014^{b}	0.335±0.035^{abc}	0.490±0.127^{de}	0.080±0.014^{bcde}	ND
T	0.435±0.021^{c}	0.210±0.000^{b}	0.205±0.021^{ab}	0.355±0.007^{abc}	0.025±0.007^{ab}	ND

*All values are means of triplicate determinations

ND = Not Detected

Mean with the same letter within a column are not significantly different at $p<0.05$

Table 1 shows the mean concentration of heavy metals in mg/kg in bread brands from distribution outlets ranged from Fe (0.315±0.021 to 1.480±0.028), Pb (0.010±0.000 to 0.66±0.014), Cr (0.085±0.035 to 1.200±0.000), Zn (0.280±0.042 to 0.510±0.099), and Ni (0.005±0.007 to 0.115±0.007). Cd was only detected in one sample and its concentration was 0.025±0.005 mg/kg.

Table 2: Mean Concentration of Heavy metals (mg/kg) in Samples from Bakeries

Samples	Concentration of Heavy Metals (mg/kg)*					
	Fe	Pb	Cr	Zn	Ni	Cd
A	0.755 ± 0.007^{j}	0.190 ± 0.014^{efg}	0.455 ± 0.007^{def}	0.435 ± 0.021^{h}	ND	ND
B	0.340 ± 0.000^{c}	0.090 ± 0.014^{bc}	0.670 ± 0.000^{f}	0.300 ± 0.014^{b}	ND	ND
C	0.640 ± 0.014^{h}	0.025 ± 0.015^{a}	0.320 ± 0.014^{abcde}	0.305 ± 0.021^{b}	ND	ND
D	0.910 ± 0.000^{m}	0.190 ± 0.014^{efg}	0.045 ± 0.014^{a}	0.405 ± 0.007^{gh}	ND	ND
E	0.540 ± 0.000^{g}	0.195 ± 0.012^{efg}	0.415 ± 0.021^{bcde}	0.355 ± 0.007^{de}	ND	ND
F	0.330 ± 0.014^{bc}	0.050 ± 0.011^{ab}	0.640 ± 0.014^{ef}	0.365 ± 0.021^{def}	ND	ND
G	0.750 ± 0.000^{j}	0.355 ± 0.050^{i}	0.285 ± 0.021^{abcd}	0.345 ± 0.021^{cd}	ND	ND
H	0.760 ± 0.000^{j}	0.125 ± 0.021^{cd}	0.255 ± 0.007^{abcd}	0.410 ± 0.0283^{gh}	ND	ND
I	0.340 ± 0.000^{c}	0.135 ± 0.007^{cde}	0.295 ± 0.007^{abcd}	0.360 ± 0.014^{de}	ND	ND
J	0.240 ± 0.014^{a}	0.200 ± 0.014^{fg}	0.465 ± 0.007^{def}	0.355 ± 0.007^{de}	ND	ND
K	0.760 ± 0.000^{j}	0.275 ± 0.035^{h}	0.255 ± 0.007^{abcd}	0.360 ± 0.014^{de}	ND	ND
L	$0.765\pm0.007\ j^{k}$	0.350 ± 0.000^{i}	0.715 ± 0.007^{f}	0.360±0.000	ND	ND

M	0.505±0.007 [f]	0.140±0.0283[cde f]	0.435±0.035cd e[f]	0.430±0.014[h]	ND	ND
N	0.800±0.000 [l]	ND	0.535±0.115de[f]	0.355±0.007[de]	0.005±0.001[b]	ND
O	0.780±0.000 [k]	ND	0.710±0.0283[f]	0.385±0.007[efg]	ND	ND
P	0.660±0.014 [i]	0.310±0.014[hi]	0.105±0.007[abc]	0.435±0.007[h]	ND	ND
Q	0.470±0.000 [e]	0.190±0.000[efg]	0.090±0.0283[ab]	0.210±0.014[a]	ND	ND
R	0.445±0.007 [d]	0.215±0.007[g]	0.110±0.014[abc]	0.220±0.014[a]	0.010±0.000[c]	ND
S	0.780±0.000 [k]	0.095±0.007[bc]	0.295±0.021[abcd]	0.395±0.007[fg]	ND	ND
T	0.315±0.007 [b]	0.160±0.014[defg]	0.100±0.000[abc]	0.320±0.014[bc]	ND	ND

Mean with the same letter within a column are not significantly different at $p<0.05$

*All values are means of triplicate determinations

ND = Not Detected

Table 2 shows the mean concentration of bread brands (A – T) collected from sampled bakeries. The mean concentrations of heavy metals (Fe, Pb, Cr, Zn, and Ni) in mg/kg ranged from Fe (0.240±0.014to 0.910±0.000), Pb (0.025±0.015 to 0.355±0.050), Cr (0.090±0.0283 to 0.715±0.007), Zn (0.210±0.014 to 0.435±0.021), and Ni (0.005±0.001 to 0.010±0.000), while Cd was not detected in any of the samples.

Table 3: Mean Concentration of Heavy Metals of Popular Flour Used in Production

Samples	**Concentration of Heavy Metals (mg/kg)***					
	Fe	**Pb**	**Cr**	**Zn**	**Ni**	**Cd**
X	0.0470±0.0014	0.0140±0.0009	0.0110±0.0005	0.0210±0.0005	0.0070±0.0010	ND
Y	0.0320±0.0005	0.0160±0.0000	0.0040±0.0009	0.0190±0.0005	0.0060±0.0005	ND
Z	0.0300±0.0014	0.0170±0.0005	0.0100±0.0005	0.0190±0.0005	0.0050±0.0010	ND

Mean with the same letter within a column are not significantly different at $p<0.05$.

*All values are means of triplicate determinations

ND = Not Detected

Table 3 shows the mean concentration of selected heavy metals in popular flour samples used by most bakers in the study area (Makurdi Metropolis). It shows the concentrations of heavy metals in mg/kg to be Fe (0.0470±0.0014), Pb (0.0140±0.0009), Cr (0.0110±0.0005), Zn (0.0210±0.0005) and Ni (0.0070±0.0010) for sample X, and sample Y has Fe (0.0320±0.0005), Pb (0.0160±0.0000), Cr (0.0040±0.0009), Zn (0.0190±0.0005) and Ni (0.0060±0.0005). In sample Z, the concentration of Fe was (0.0300±0.0014), Pb (0.0170±0.0005), Cr (0.0100±0.0005), Zn (0.0190±0.0005) and Ni (0.0050±0.0010). Cd was not detected in the respective samples.

Table 4: Comparison between mean concentrations of selected heavy metals in this study with permissible limits from standard organizations

Samples	Concentration of Heavy Metals (mg/kg)*					
	Fe	**Pb**	**Cr**	**Zn**	**Ni**	**Cd**
A	1.335 ± 0.021^{j}	0.425 ± 0.007^{f}	0.835 ± 0.191^{fgh}	0.455 ± 0.021^{cde}	0.005 ± 0.007^{a}	ND
B	0.880 ± 0.014^{g}	0.440 ± 0.014^{f}	0.730 ± 0.0424^{defgh}	0.360 ± 0.057^{abcd}	0.095 ± 0.007^{cde}	ND
C	0.685 ± 0.0212^{e}	0.23 ± 0.000^{bc}	0.295 ± 0.035^{abc}	0.390 ± 0.057^{abcde}	0.100 ± 0.000^{de}	0.025 ± 0.005^{b}
D	1.480 ± 0.028^{l}	0.41 ± 0.000^{f}	0.085 ± 0.035^{a}	0.510 ± 0.099^{e}	0.115 ± 0.007^{e}	ND
E	0.760 ± 0.000^{f}	0.66 ± 0.014^{g}	0.650 ± 0.000^{cdefg}	0.410 ± 0.014^{abcde}	ND	ND
F	0.665 ± 0.007^{e}	0.415 ± 0.021^{f}	1.075 ± 0.035^{hi}	0.415 ± 0.021^{bcde}	0.110 ± 0.014^{e}	ND
G	0.775 ± 0.021^{f}	0.355 ± 0.007^{e}	0.365 ± 0.035^{abcd}	0.375 ± 0.35^{abcd}	0.105 ± 0.007^{e}	ND
H	1.225 ± 0.021^{i}	0.420 ± 0.014^{f}	0.360 ± 0.014^{abcd}	0.475 ± 0.050^{cde}	0.015 ± 0.021^{a}	ND
I	0.370 ± 0.000^{b}	0.34 ± 0.042^{e}	0.385 ± 0.021^{abcd}	0.385 ± 0.021^{abcde}	0.115 ± 0.021^{e}	ND
J	0.475 ± 0.035^{d}	0.340 ± 0.028^{e}	0.495 ± 0.021^{bcdef}	0.410 ± 0.057^{abcde}	0.100 ± 0.000^{de}	ND
K	0.315±0.021a	0.360 ± 0.014^{e}	0.360 ± 0.000^{abcd}	0.400 ± 0.014^{abcde}	0.100 ± 0.000^{de}	ND
L	1.390 ± 0.000^{k}	0.415 ± 0.021^{f}	1.200 ± 0.000^{i}	0.435 ± 0.050^{cde}	0.065 ± 0.018^{abcde}	ND

M	0.740±0.000^{f}	0.450±0.000^{f}	0.980±0.014^{ghi}	0.470±0.042^{cde}	0.08±0.011^{bcde}	ND
N	1.215±0.021^{i}	0.345±0.021^{e}	0.665±0.021^{cdefg}	0.430±0.071^{bcde}	0.005±0.07^{a}	ND
O	0.880±0.014^{g}	0.010±0.000^{a}	0.750±0.014^{efgh}	0.400±0.028^{abcde}	0.035±0.015^{abcd}	ND
P	0.870±0.000^{g}	0.415±0.021^{f}	0.130±0.014^{ab}	0.470±0.042^{cde}	0.095±0.007^{cde}	ND
Q	0.500±0.014^{d}	0.255±0.021^{c}	0.125±0.007^{ab}	0.280±0.042^{a}	0.090±0.014^{cde}	ND
R	0.650±0.000^{e}	0.295±0.007^{d}	0.175±0.035^{ab}	0.300±0.071^{ab}	0.030±0.028^{abc}	ND
S	1.125±0.007^{h}	0.200±0.014^{b}	0.335±0.035^{abc}	0.490±0.127^{de}	0.080±0.014^{bcde}	ND
T	0.435±0.021^{c}	0.210±0.000^{b}	0.205±0.021^{ab}	0.355±0.007^{abc}	0.025±0.007^{ab}	ND
Permissible Limits						
WHO (2001)	18mg/day	0.2mg/kg	0.3mg/kg	0.2 mg/kg	5 ug/kg/day	0.2 mg/kg

*All values are means of triplicate determinations

DISCUSSION

Heavy metals are the most common environmental pollutants in the world (Soetan *et al.,* 2008).The exhibition of toxic properties by heavy metals leads to metal poisoning, which has adverse effects on human and ecosystem's health (Arora *et al.,* 2008). Although acute poisoning from heavy metal poisoning is rare through ingestion or absorption via the skin, chronic exposure even in small concentrations can be disastrous (Rana, 2011). Chronic exposure to heavy metals leads to accumulation in the food chain which leads to an increased stock in biota, therefore magnifying the human dose (Bando *et al*., 2023).

Although some of the studied heavy metals such as Fe, Zn, Ni and Cr are essential in human nutrition, their determination in food products is imperative, since they pose health risks at high concentrations. In the present study, bread loaves contained varying concentrations of heavy metals, with exception of Cd which was only present in sample C (from distribution outlet). The concentration of heavy metals in the studied samples from the bakeries and distribution outlets followed the sequence, Fe > Zn > Cr >Pb> Ni > Cd.

Zn and Fe happen to be among the metals/minerals that Nigerian government, and some other governments around the globe mandated that they be used to fortify wheat flour (a major component of bread). Zn had the lowest and highest mean concentrations in mg/kg in sample Q (0.210±0.014) and sample A (0.435±0.021)and in bread loaves from bakeries, while that from the distribution outlet were relatively higher, 0.280±0.042 (in sample Q) and 0.510±0.099(in sample D) respectively. When these highest and lowest values of Zn were compared with values reported in literature, the values were found to be lower than 3.26±0.06 and 1.18±0.03 mg/kg reported by Doe *et al.,* (2013) in bread. It was also lower than the reports in bread loaves from Khalid and Rehman, (2013), Khaniki *et al.,* (2005), and Gholam and Khaniki, (2005), which were 2.96 - 4.60, 12.77 - 19.27, 10.42 - 14.25, 2.23 -6.63mg/kg respectively. It was found to be lower than the concentration of Zn in wheat flour as reported by Doe *et al.,* (2013) (6.314±0.211 and 6.154±0.313 mg/kg), by Agu *et al.,* (2010) (24.13±2.19 mg/kg).This is an indication that bakers in Makurdi are not fortifying their bread as required by standard organizations such as NAFDAC. The concentration of Zn in this study is in concordance with report by Magomya *et al.,* (2013).

The lowest and highest mean concentration of Fe in bread loaves obtained from bakeries and distribution outlets ranged from (0.240±0.014 - 0.910±0.00mg/kg) and (0.315±0.021 - 1.480±0.028mg/kg) respectively. These results are within the range of those reported by Magomya *et al.,* (2013) (0.098 - 0.53 mg/kg) and with the value of one of the samples reported by Agu *et al*., (2010), while the values of other bread samples in their studies were higher. The report by Doe et al., (2013) (2.26 - 2.82 mg/kg), Khalid and Reman, (2013), (177.3 and 32.9 mg/kg), and 49.8 – 59.21 mg/kg by Jawad *et al.,* (2012) were contrary to those from this study.

Zn and Fe are the two most abundant heavy minerals in the human body, with Zn (1.5–2.5 g) and Fe (3–4 g) present in the average adult. These metals are frequently assessed together, because they share common dietary sources (Kordas and Stoltzfus, 2004; Sandstead, 2000; Hunt, 2003). Their absorption from food is believed to be enhanced and inhibited by similar compounds (Sandstead, 2000; Nair *et al.,* 2013), and consequently, deficiency of both nutrients is thought to occur simultaneously.

The mean concentration of Cr from this study ranged from 0.090±0.0283 – 0.715±0.007 mg/kg in bread loaves from bakeries, and 0.085±0.035 – 1.200±0.000 mg/kg in bread loaves obtained from distribution outlets. The highest value of heavy metals recorded in this study is slightly below that reported by Naghipour *et al.,* (2014) (1.3 mg/kg). The Cr found in the analysed samples could have originated from whole wheat and brown sugar (Rana *et al.,* 2011), and other ingredients used in the making of bread. Also, the type of technology used in the baking process can increase the concentration of Cr in the finished product, as compared to the raw product (Magomya *et al.,* 2013).

Cr is an important heavy metal which is relevant in human nutrition for healthy living, and has a wide range of industrial applications. According to Rana *et al.*, (2011), Cr has the ability to reduce blood glucose, and is used to control certain cases of diabetes. While industrially it can be used in electroplating, metal finishing, magnetic tapes, pigments, leather tanning, wood protection, chemical manufacturing, brass, electrical and electronic equipment and catalysis.

Pb is one of the leading carcinogenic heavy metals that find their way into the human body via dietary intake and other means of exposure. The concentration of Pb in this study ranged from 0.025±0.015 –0.355±0.050 mg/kg (bread loaves from bakeries), and 0.010±0.000 – 0.66±0.014 (bread loaves from distribution outlets). This values were in agreement with ranges recorded by Khaniki *et al.,* (2013) (0.27 – 0.52 mg/kg) and Agu *et al.,* (2010) (0.03 – 0.10 mg/kg). While Doe *et al.*, (2013) had lower concentrations of 0.0051 – 0.0050 mg/kg, contrastingly higher concentrations were recorded by Dada *et al.,* (2017) (1.26±0.01 mg/kg), Magomya *et al.,* (2010) (3.13 mg/kg), Alomary and Wedian, (2012) (264.2 mg/kg), and Odunwo and Konne, (2014) (7.28±2.14 mg/kg).

Ni, an essential heavy metal, whose specific function in the human system is unknown, but it is known to be present in many enzymes in the body. Ni was detected only in two samples obtained from bakeries, with concentration of 0.005±0.001 and 0.010±0.000, but it concentration ranged from 0.005±0.007 – 0.115±0.007 mg/kg in bread loaves from distribution outlet (except for sample E); where it was not detected. Cd was not detected in the bread loaves from bakeries, but it was detected only in sample C from distribution outlet. The concentration of heavy metals in BFB and BFD varied significantly at $p<0.05$. The study also revealed that the heavy metals concentrations were lower in flour samples when compared with the baked bread from distribution outlets and factories.

CONCLUSION

The study established the presence of the selected heavy metals in frequently consumed bread loaves baked and sold in Makurdi metropolis, Benue State. This is as a result of activities such as handling, packaging, transporting, and environmental conditions around the distribution out lets. The type of technology used in bread production influences the stock of heavy metal in the finished product.

It further showed that flour which is the major ingredient in bread making contains heavy metals, but the concentration in the finished product showed that other ingredients, additives, kneading, baking, and distribution processes contribute significantly to the stock of heavy metal in the finished product.

Recommendations

The contamination of bread loaves by heavy metals can be mitigated by replacing old pans and equipment with Best Available Technology (BAT), and employing Standard Operating Procedures (SOP) in production processes.

Regular monitoring by public health department and NAFDAC should be done to ascertain the safety of food from heavy metals.

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