HEAVY METALS CONTENT OF COMMERCIALLY SOLD FERMENTED MILK PRODUCTS IN AKURE MARKETS, SOUTH-WEST, NIGERIA.

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ABSTRACT

The study investigated the quantitative presence of heavy metals in samples of yoghurt (fermented milk) commercially available in Akure market, South-west Nigeria. Fifteen random samples plain, sweetened, and flavoured yoghurt of different variants were analyzed. The heavy metals Zinc, Chromium, Copper, Cadmium, Lead and Iron were analysed for using the Atomic Absorption Spectrometry (AAS). The study revealed that Cd value in the samples was below 0.0004mg/l, lowered than the Standards Organization of Nigeria (SON) and World Health Organization (WHO) maximum permitted level 0.003mg/l. In the samples, Pb value was 0.022±0.001mg/l. This value was higher than the WHO and SON stipulated maximum value 0.01mg/l. Iron, lowest quantity detected was 0.981±0.053mg/l in the samples which showed a significantly higher value than the upper limit 0.3mg/l standard by WHO and SON. The highest quantity of Fe 2.595±0.156mg/l in one sample was very high. Zinc detected in the samples 0.226±0.011mg/l and 0.413±0.0017mg/l, lowest and highest values respectively are far below the maximum permitted limit of 3mg/l. Chromium in the samples 0.26mg/l indicated least value which is much higher than the maximum limit of 0.05mg/l by WHO and SON. Copper indicated least value of 1.571 ± 0.016 mg/l which is above the WHO maximum limit of 1 mg/l, but within the maximum limit of SON, 2mg/l. However, the highest value 5.174±0.207mg/l obtained is far above the permissible limits. The effects of accumulation of heavy metals in the human system are serious health hazards, thereby, prolonged consumption of all the commercially sold fermented milk product samples used in the study constitute a high health risk to the consuming public. Government agencies saddled with the statutory functions of regulations and enforcement must up-scale their monitoring and enforcement activities to protect the consumers.

Keywords: Heavy metals, Yoghurt, Fermented milk Samples, Analyzed.

INTRODUCTION

Metal toxicity incidences have greatly amplified the need for ecological and health risk assessment in the various media where it can be contacted, such as food and environmental samples. Metal toxicity is defined as the toxic effect of certain metals in certain forms and doses on life (Yovana, 2016). Metal toxicity is attributed to the presence of heavy metals in the environment in considerably high amounts. Increased industrial activities has led to more pollution and contamination, as well as increased exposure levels to poisoning substances in the industry, its products and surrounding areas. Heavy metals are metals with specific gravity of 5g/ml or more. These are found mostly in groups III-V of the periodic table (John, 2002). These metals cause environmental pollution(heavy metals pollution), from a number of sources including Lead in petrol, industrial effluents and leaching of metal ions from the soil into lakes and rivers, as well as acid rain, with a great potential harm to humans and other life forms (Nnonah, 2009)the heavy metals have high risk impacts due to their toxicity, abundance, persistence, and subsequent bioaccumulation in organisms (Barlas*et al.*, 2014; Yi *et al.*, 2011; Zhu *et al.*, 2012; Fu *et al.*, 2014; Yovana*et al.*, 2016).

The entry of these into the environment is through sources/means such as run-off or waste from the purification of metals, production of processing plants, waste and effluent from

electro-plating, sludge sedimentation tanks etc (Yovana, 2016). They exist as metals in nature by forming positive ions when combined with other ions in compounds and exhibit general characteristics of metals when in pure bulk form. The metals include Lead, Chromium, Manganese, Mercury, Arsenic, iron, Zinc, Copper and Cadmium. Dairy products like yoghurt are a regular consumer product (Sylvester *et al.*, 2011), therefore, monitoring of contaminants such as heavy metals and pesticide residue is very important. Fermented milk is the generic term for any milk that has undergone modifications by microorganisms, notably lactic acid producing bacteria. Milk is obtained from animals such as goats, cows, and buffaloes, and processed into powder milk, cream, evaporated milk and fermented products. In industrial production of fermented milk, powder milk is often used and inoculated with starter cultures of fermentative microorganisms. However, traditional fermented milk products in Nigeria include Nunu (a sour milk), Kindiriomo (sour yoghurt), Cuku (Fulani cheese), Maishanu (a local butter) and Wara (Yoruba cheese) (Egwimet al., 2009). I ndustrial products of fermented milk may be plain, sweetened with sucrose or fruit syrup, and/or flavoured (Tanime and Robinson, 1999). The consumption of fermented milk products has always been on the increase globally because of population increase, industrial development and consumer behavior (Chanda and Kilara, 2001). Data for consumption in Nigeria is not available, but the surge and saturation of the market by such products are possibly testimonials to an increase. The presence of Lead, Cadmium, and other heavy metals in dairy products and fermented milk could be from the natural amount present in the milk from source, handling, processing, fermentation and packaging activities, including packaging materials.

The aim of this study is to assess the heavy metals content of commercially sold fermented milk products in Akure, South-west Nigeria.

MATERIALS AND METHODS

Samples collection and handling:

Fifteen commercially available brands of yoghurt drinks in plastic bottles were randomly obtained from a market in Akure, South-west Nigeria. Each sample was checked for NAFDAC approval marks, manufacturers' address, production and expiry dates, ingredients, packaging methods and registration status. All the samples carried the NAFDAC approval numbers as at the time of the study. They were also within the declared shelf-life periods. Samples were immediately transferred into a refrigerator in the laboratory for preservation before analyses.

Heavy metals analyses

The heavy metals determination was carried out in the laboratory of Federal University of Agriculture, Akure (FUTA), using the Atomic Absorption Spectrometer (Buck Scientific Model 210 VGP). The samples were digested according to the method of Bingal et al. (2010). Validation of samples readings was ensured in triplicates. A series of standard solutions were prepared in distilled de-ionized water for instrumental calibration. Standard and blank samples were analyzed for every ten samples analyzed.

Data Analyses

Mean values of triplicate readings and standard deviations were calculated.



Sample	Cr (mg/l)	Cu (mg/l)	Zn (mg/l)	Cd (mg/l)	Pb (mg/l)	Fe (mg/l)	/	
PY1 PY2 SY1 SY2 PSY1 AfY1 AfY2 AfY3 SfY1 SfY2 PfY VfY BfY	0.260 ± 0.011 0.351 ± 0.017 0.431 ± 0.019 0.404 ± 0.016 0.358 ± 0.016 0.456 ± 0.018 0.405 ± 0.016 0.311 ± 0.012 0.353 ± 0.016 0.260 ± 0.013 0.355 ± 0.017 0.302 ± 0.012 0.415 ± 0.017	5.174 ± 0.207 4.601±0.184 3.286±0.141 3.261±0.129 2.702±0.110 3.241±0.130 3.233±0.135 3.531±0.150 1.571±0.067 2.626±0.110 2.712±0.106 3.828±0.140 3.267±0.136	0.226 ± 0.011 0.277 ± 0.013 0.246 ± 0.010 0.377 ± 0.019 0.413 ± 0.017 0.356 ± 0.018 0.251 ± 0.013 0.355 ± 0.017 0.364 ± 0.020 0.403 ± 0.020 0.403 ± 0.020 0.403 ± 0.016 0.377 ± 0.016	BDL BDL BDL BDL BDL BDL BDL BDL BDL BDL	0.022 ± 0.001 0.030 ± 0.001 0.048 ± 0.002 0.032 ± 0.001 0.029 ± 0.001 0.044 ± 0.003 0.029 ± 0.002 0.037 ± 0.002 0.031 ± 0.001 0.029 ± 0.001 0.041 ± 0.002 0.045 ± 0.002	$\begin{array}{c} 1.726 \pm 0.104 \\ 0.998 \pm 0.060 \\ 1.962 \pm 0.118 \\ 2.054 \pm 0.123 \\ 2.595 \pm 0.156 \\ 1.522 \pm 0.091 \\ 2.107 \pm 0.126 \\ 2.541 \pm 0.152 \\ 0.981 \pm 0.053 \\ 2.057 \pm 0.123 \\ 2.489 \pm 0.143 \\ 1.420 \pm 0.085 \end{array}$	RESULTS DISCUSSION	AND
OfY SpY	0.361±0.019 0.402±0.020	3.930±0.157 4.076±0.131	0.326±0.016 0.275±0.014	BDL BDL	0.043±0.002 0.031±0.001	2.049±0.123 1.035±0.062		

PY= Plain Yoghurt, SY= Sweetened Yoghurt, PSY= Plain Sweetened Yoghurt, AfY= Apple flavoured Yoghurt, SfY= Strawberry flavoured Yoghurt, PfY= Pineapple flavoured Yoghurt, VfY= Vanilla flavoured Yoghurt, BfY= Banana flavoured Yoghurt, OfY= Orange flavoured Yoghurt, SpY= Super plain Yoghurt, BDL = Below Detection Limit.

Table 1.0. Metal contents of samples.

	Cr	Cu	Zn	Cd	Pb	Fe
	(mg/l)					
Mean	0.362	3.402	0.337	0.000	0.036	1.769
S.D.	0.059	0.867	0.065	0.000	0.008	0.581
Minimum	0.260	1.571	0.226	0.000	0.022	0.981
Maximum	0.456	5.174	0.413	0.000	0.048	2.595

Table 3.0 Maximum Permitted Levels (MPL) of heavy metals defined by the WHO and SON



Heavy	WHO	SON (mg/l)
metal	(mg/l)	
Cr	0.05	0.05
Cu	1.00	1.00
Zn	5.00	5.00
Cd	0.003	0.003
Pb	0.01	0.01
Fe	0.03	0.03

For Copper, WHO and SON Maximum Permitted limits are documented at 1mg/l and 2mg/l respectively (Table 3.0). This study recorded the lowest Copper content at 1.571mg/l in sample SfY. This is higher than the maximum limit by WHO but lower than that of SON.

All other samples exhibited values higher than the permitted limits by both regulatory agencies, with the peak at 5.174mg/l in sample PY1. Other workers have reported Copper in beverages exceeding the Maximum Permitted limits (Adegbola *et al.*, 2015; Izah *et al.*, 2016; Salako *et al.*, 2016). Magomya *et al.* (2015) and Ogunlana *et al.* (2015), reported some beverage drinks, including yoghurt, containing Copper within the permitted limits, in Nigeria.

The results of this study revealed that the fifteen commercially available yoghurt sample examined do not pose health risk due to Cadmium and Zinc. The levels of the other metals, notable Chromium, Copper, Iron and Lead are however, higher in some or most of the samples than the permitted levels. Since yoghurt is a product with good share of the market, the public may be at risk consuming these products in large quantities per serving. Appropriate government and regulatory agencies responsible for monitoring and enforcing regulations need to intensify efforts to protect public health. Further research on the topic could be carried out on up-scale to verify, extend or validate the findings of this study.

Cadmium concentration obtained in all the samples were below detection limit of 0.0004mg/l (Table1.0), which is much lower than the Maximum Permitted Level of 0.003mg/l by the WHO and SON. This observed result is similar to the report of Adetunji et al. (2013). The report showed a result of 0.0019mg/l for Cadmium in yoghurt. It also falls in line with the general trends observed for food drinks, yoghurt and beverages in Nigeria (Adepoju-Bello et al., 2012; Emgwa et al., 2015; Magomya et al., 2015; Salako et al., 2016). Yabrir et al. (2016), in the study of heavy metals in ruminant animals, reported that Cadmium in ewe and goat milk were below the permissible limits, though, ewe milk showed higher content than goat milk. This was attributed to different locations of feeding of the animals. Cadmium in milk might have natural or anthropogenic origins fertilizers and atmospheric deposition in soil - (Maas et al., 2011) and is considered as an industrial risk (Massanyi et al., 1995). Cadmium is ranked among the most toxic heavy metals (Dana, 2014). In human body, Cadmium accumulates in liver and kidney and causes renal damage and dysfunction (Salah et al., 2013). Prolonged and continuous consumption of milk or milk products with high level of Cadmium by humans lead to bioaccumulation of the metal and major health hazards. Cadmium is more known by its toxicity and metabolic antagonism with Zn and other elements. Contamination of pastures with Cd can increase the content in grasses for about 40 times. Some plants (e.g. oat) have the ability to concentrate cadmium received from the soil (Qin *et al.*, 2009). According to Zaidi and Wani (2012), inflammation symptoms may occur several hours after exposure and include cough, dehydration, nose and throat irritation, headache, dizziness,

weakening, chest pain. The result of this study indicated that there could be no risk due to Cadmium poisoning to the consumers of any of the particular batches of the products analysed.

Lead values obtained in the samples ranged from 0.022mg/l in sample PY1 to 0.048mg/l in sample SY1 (Table 1.0). Both values are above the maximum limits stipulated by the WHO and SON (Table 2.0). In beverages in Nigeria, Lead has been found above the Maximum Contaminant Levels both for alcoholic and non-alcoholic drinks (Adegbola et al., 2015; Engwa et al., 2015; Magomya et al., 2015; Ogunlana et al., 2015). However, it has also been found in concentrations below the permitted limits by Adepoju-Bello et al. (2012) and Iweala et al. (2014). However, in milk study by Yabrir et al., (2016), Lead content in ewe milk was found to be higher in the mountain region goat milk owing to differences in location, where it was identified that the mountain region was less prone to industrial pollution than the plain region. The vegetation in the mountain region could carry less pollutants than that of the mountain region. This indicated that feedstock is a major factor that introduces heavy metals into the milk of ruminants, and the initial concentration of these metals in the raw milk is a determinant of the presence of the metals in fermented products. Lead is poorly absorbed by mammals and their concentrations in milk are generally low and milk is not considered as an important source of exposure (Casey *et al.*, 1995). Lead intoxication in humans is known since the second century. Cardiovascular, hematological and neurological problems occur even in exposures to low quantities. Problems in urinary, digestive, hepatic and immune system occur when exposed to higher levels (US National Research Council, 2005).

The lowest values obtained for Iron determination in the samples was 0.981mg/l while the highest was 2.595mg/l. the maximum limit set by SON is 0.03mg/l. All the samples analyzed in this study contained Iron much higher than the maximum limit stipulated by regulations in Nigeria. The finding is in tandem with the general trend observed by other researchers in yoghurt, milk and other food drinks and beverages in Nigeria (Sylvester *et al.*, 2011). Prolonged consumption of all the fermented milk products analyzed can lead to iron toxicity by bio-accumulation in the human organs. This poses a health risk. Iron toxicity can be either sudden or gradual. Many serious health problems may be caused by accidental overdoses, taking high-dose food products for a long time, or chronic iron overload disorders. Gradually, the excess iron accumulates in internal organs, causing potentially fatal damage to the brain and liver (www.healthline.com, 2018).

The level of Zinc is lowest at 0.226mg/l and is highest at 0.413mg/l, which is by far below the Maximum Permitted level of 3mg/l by WHO and SON (NIS 554:2007; WHO, 2011). Findings by Udota and Umuodafia (2011), Ubuoh (2013), Ogunlana *et al.* (2015) and Salako *et al.* (2016) documented similar trend in studies on food drinks and beverages, including yoghurt, in Nigeria. Jigam *et al.* (2011), observed that Zinc in fresh cow milk was lower than in goat milk as reported by Park (2000). The observed quantities of 0.35mg/l, 0.25mg/l and 0.40mg/l were far below the Maximum permitted limits by WHO and SON. Zinc is an essential trace element, necessary for

the functioning of several enzyme's systems, but excessive quantities of zinc coming from geological sources adversely affects water and food quality. Zinc toxicity symptoms include vomiting, dehydration, abdominal pain, nausea, lethargy, dizziness and muscle's incoordination (Bahtir and Alush, 2014). All the samples analysed in this study pose no risk of Zinc toxicity. Chromium content in the samples was observed to be lowest at 0.260mg/l in both samples PY1 and SfY2, although, it is higher than the Maximum Permitted of 0.05mg/l by the WHO and SON. A highest value of 0.456mg/l was obtained in samples AfY1. Adegbola *et al.* (2015), reported the same trend in the work done. Also, Yabrir *et al.* (2016) reported low values of Chromium in ewe milk but higher values than the stipulated permissible levels in goat milk. Chromium is considered as essential trace element (Bowen, 1979) but it can be a poison at higher level (Qin *et al.*, 2009). Chromium compounds are mutagenic and carcinogenic in variety of test systems (Zodape *et al.*, 2012). However, it is essential to maintain the metabolic systems of human body (Qin *et al.*, 2009) and plays a role in sugar metabolism as a cofactor with insulin (Hoekstra *et al.*, 1970).

In conclusion, all the commercially sold fermented milk products analyzed showed no risk of health hazard of Zinc and Cadmium poisoning to the consuming populace. However, all the samples exhibited high values of Lead, Chromium, Copper and Iron above the permitted levels by WHO and SON. This implies that continuous consumption of the batches of these products by the public exposes them to grave health hazards of heavy metals toxicities. All relevant government agencies in the country are advised to increase their monitoring and surveillance of milk and fermented milk products in the country for safety of public health.

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