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Assessment of Heavy Metal Contents in Raw Cow Milk Samples from Selected Local Government Areas in Kano State, Nigeria

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Abstract - **The study assessed the concentration of copper (Cu), Lead (Pb), Zinc (Zn) and Iron (Fe) in cow milk samples (raw) got from selected Local Government Areas, Kano State namely; (Gwale (Sample Location A), Dala (Sample Location B) and Ungogo (Sample location C) within Kano state, Nigeria. Heavy metal determination was done according to standard produres. Heavy metal concentrations (Cu, Fe, Zn, and Pb) were assessed by the use of Atomic Absorption Spectrometer (AAS). The content of Copper (Cu) in the sample of cow milk from the three Local Government (Gwale, Dala and Ungogo) were 0.0584 mgl^{-1}, 0.0714 mgl^{-1} and 0.2604 mgl^{-1} respectively. The concentration of Zinc (Zn) in the raw cow milk samples from the three Local Government (Gwale, Dala and Ungogo) were 0.1336 mgl^{-1}, 0.1148 mgl^{-1} and 0.1595 mgl^{-1} respectively. The levels of Iron (Fe) from the samples of cow milk (raw) from the selected Local Government areas (Gwale, Dala and Ungogo) were 0.7319 mgl^{-1}, 0.6438 mgl^{-1} and 0.8709 mgl^{-1} respectively. The levels of Lead (Pb) from the selected Local Government areas (Gwale, Dala and Ungogo were 0.0350 mgl^{-1}, 0.0390 mgl^{-1} and 0.4100 mgl^{-1} respectively. The result shows that the Fe and Pb concentrations in raw cow milk samples collected from all the three Local Government areas (Gwale, Dala and Ungogo) were all above the WHO permissible limits. However, the concentrations of Zn and Cu in the cow milk samples (raw) obtained from the area remained within the World Health Organization (WHO) permissible limit. Routine and further study is required to determine the heavy metals status in cow milk from other LGAs of the State to ascertain the safe levels of cow milk products to consumers in the area.**
Keywords: **Heavy Metals, Milk, Contaminant, Food Safety, Kano**

I. INTRODUCTION

Milk is a source of vitamins that is required for appropriate growth and functioning of various body organs and tissues. It is a crucial requirement in nutrition and its intake has increased recently [7]. The harmful effect of over dosage of these vitamins and mineral in human body is of concern [5]. [12] reported Cadmium, Lead, Chromium, Nickel, Mercury and Arsenic as the most common toxic heavy metals of concern based on their contamination reports in herbal preparations, Chromium is linked with cardiovascular diseases and diabetes.

Cadmium is considered a metal that can negatively impact the quality of agricultural food. It is mobile within the soil-plant system and is primarily introduced to the soil through metal working industries. The presence of cadmium can lead to various toxic symptoms in plants, including effects on growth, effects on photosynthetic abilities of plants, deactivation of enzymes and plant-water interactions interference [8].

Most vital micro-nutrients are essential in the bio-chemical roles in living organisms, these micro-nutrients are integral components of various enzymes [16]. However, excessive intake of these micro-nutrients can lead to toxicity, and the level of toxicity varies depending on the element and species [17]. The potential contamination of milk by heavy metals can occur when lactating cows are exposed to pollution or consumes contaminated feeds and water. Additionally, the manufacturing process of dairy products can also contribute to contamination, as toxicants may be included during production [4], [14].

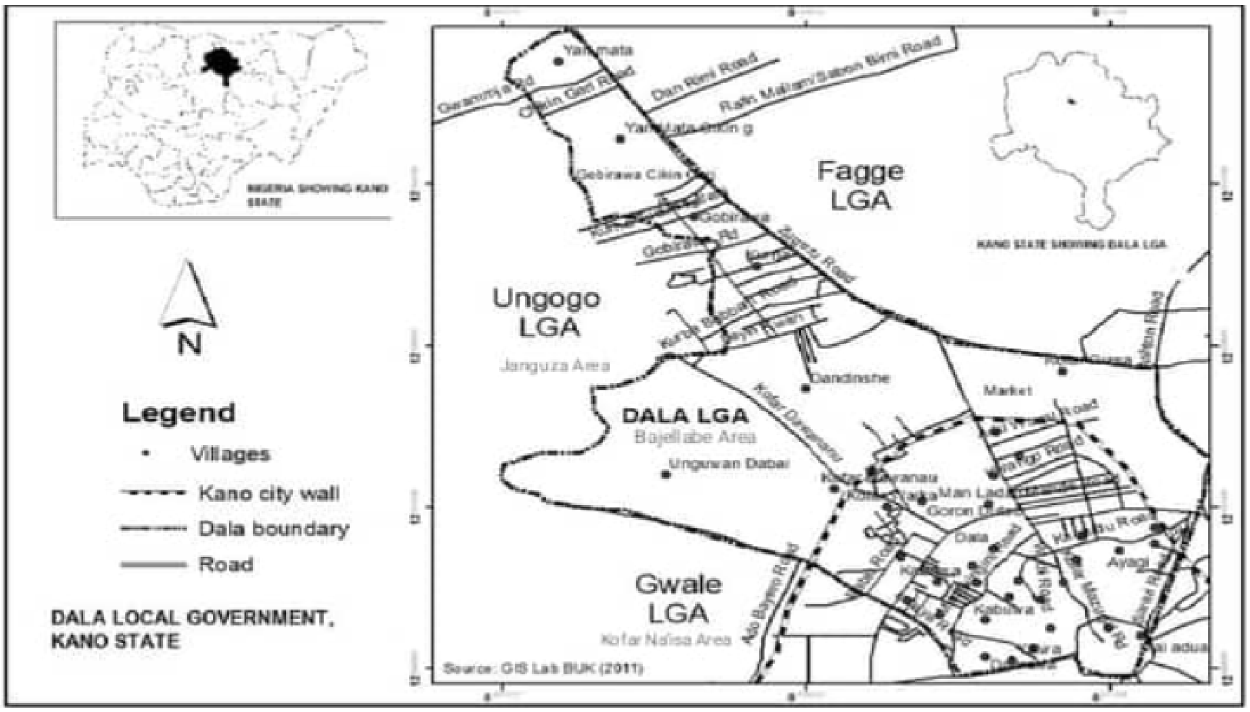
The chemical composition of dairy products is influenced by various factors as reported by [15]. These factors include the type of treatment performed on the milk, the content of the raw milk, the duration of storage and the type of packaging containers used. These factors are to be considered because they can potentially affect the composition and total quality of dairy products. Lead is particularly reported for its harmful impacts on brain development. On the other hand, Cadmium can cause various complications such as anemia, reproductive failure, renal problems, and other health issues [11].

The Flame Atomic Absorption Spectrometer (AAS) is a commonly used method for determining metal analysis. This method is effective because it minimizes interference from other elements by focusing on a specific emission spectra line for each element. AAS allows for accurate determination of trace amounts of one element even in elevated concentrations of other elements [10].

II. METHODOLOGY

A. Study Area

Kano State is one of the Northern States in Nigeria. The location of Kano lies between latitudes 13°N and 11° and longitudes 10°W and 8°E. Kano has an average elevation of 472.45m above the sea level. Kano is surrounded by neighboring states such as Katsina to the Northwest and Kaduna to the Southwest of Kano. It shares boundary to the South East by Bauchi state. Kano State has highest population of residents in Nigeria according to 2006 National Census and as reported by the National Bureau of Statistics. Kano State is a commercial state where other States obtain goods from no wonder it is referred to as the "Centre of commerce". As reported by [2], Kano has a dual climate experiencing both the dry and rainy season. The rainy season mostly beginning in May and extends through mid-October with August as the month with highest rain while the dry season extends from mid-October to May of another year [2]. The mean annual temperature is 26°C and the mean rainfall is between 800mm to 900mm.



Source: GIS Laboratory BUK, 2011

Fig. 1 Map showing location of the study area in Kano State, Nigeria

B. Sampling Area

The study was carried out in Kano State, Nigeria. All experimental works were performed at the popular higher institution in the State "Bayero University Kano known as (BUK)". Sample preparation, and digestions, including pH analysis, Moisture content analysis and Ash content analysis were done at the Chemistry Laboratory and Biochemistry Laboratory Department. The department of Soil Science and central laboratory of Bayero University Kano (B.U.K) were used for Stock solutions preparation and determination of heavy metal analysis.

C. Materials

The study ensured the accuracy of its result by calibrating all the equipment and instruments used before and during the experiments. To remove any heavy metal residue on the glassware surfaces, a 10% concentrated hydrochloric acid (HCL) solution was used for cleaning. Apparatus like measuring cylinders, digestion flasks and volumetric flasks were carefully washed with soap and water, then thoroughly rinsed with distilled water and allowed to dry.

D. Collection Procedure of Cow Milk

Five (5) milk samples (raw) were collected from five different cows randomly from three different locations of different local government in Kano State, making a total of fifteen cow's milk samples in all. In which five cow's milk samples were collected at Gwale Local Government (Kofar Na'isa Area), five were also collected at Dala Local Government (Bajallabe Area) and the last five milk samples were collected from Ungogo Local Government (Janguza Area). 1 litre of cow milk (raw) were obatined from each cow in the morning around 5:30 am and taken immediately to the laboratory for analysis.

E. Digestion Procedure

The digestion Procedure adopted in the study involved measuring 2ml each of the raw milk sample which was made to digestion using five (5) ml of concentrated HCl and five (5) ml of concentrated perchloric acid ($HClO4$) which was left for 3 hours at a temperature of 210°C. After this, the concentration of the following heavy metals particularly Copper, Lead, Zinc and Iron were determined by the use of flame AAS.

F. Statistical Procedures

Statistical Package for Social Sciences (SPSS version 23) was used to analyzed data by computing the mean and standard deviation.

III. RESULTS AND DISCUSSIONS

Table I below shows the key table of the sampling location where milk samples were taken for easy identification. Table II below shows the average concentration of heavy metals (mg/l) in the cow milk (raw) taken from the cows. Table III shows the average concentration of heavy metals in cow milk (raw) in comparison with WHO Limit. Figure 2 presents the visualization relationship between the concentration of heavy metals in cow milk (raw) from the sampling locations as compared with the WHO recommended limit.

TABLE I KEY TABLE SHOWING THE SAMPLING LOCATION.

Milk Samples Location	Sampling points
Gwale local government Area (A)	(Kofar Naisa Area)
Dala local government Area (B)	(Bajellabe Area)
Ungogo local government Area (C)	(Janguza Area)

TABLE II AVERAGE CONCENTRATION OF HEAVY METALS IN COW MILK (RAW) SAMPLES

Sample location	Heavy metals concentration (mgl^{-1})			
	Copper	Zinc	Iron	Lead
A	0.0584±0.0019	0.1336±0.0028	0.7319±0.0029	0.0350±0.0110
B	0.0714±0.0004	0.1148±0.0001	0.6438±0.0044	0.0390±0.0262
C	0.2604±0.0019	0.1595±0.0007	0.8709±0.0036	0.4100±0.0063

TABLE III AVERAGE CONCENTRATION OF HEAVY METALS IN COMPARISON WITH WHO PERMISSIBLE LIMIT

Metallic mean concentration(mg/l)	Copper (Cu)	Zinc (Zn)	Iron (Fe)	Lead (Pb)
Location A	0.0584	0.1336	0.7319	0.0350
Location B	0.0714	0.1148	0.6438	0.0390
Location C	0.2604	0.1595	0.8709	0.4100
WHO Limit (mg/l)	1.0000	5.0000	0.0300	0.0100

*WHO limit adapted from [3]

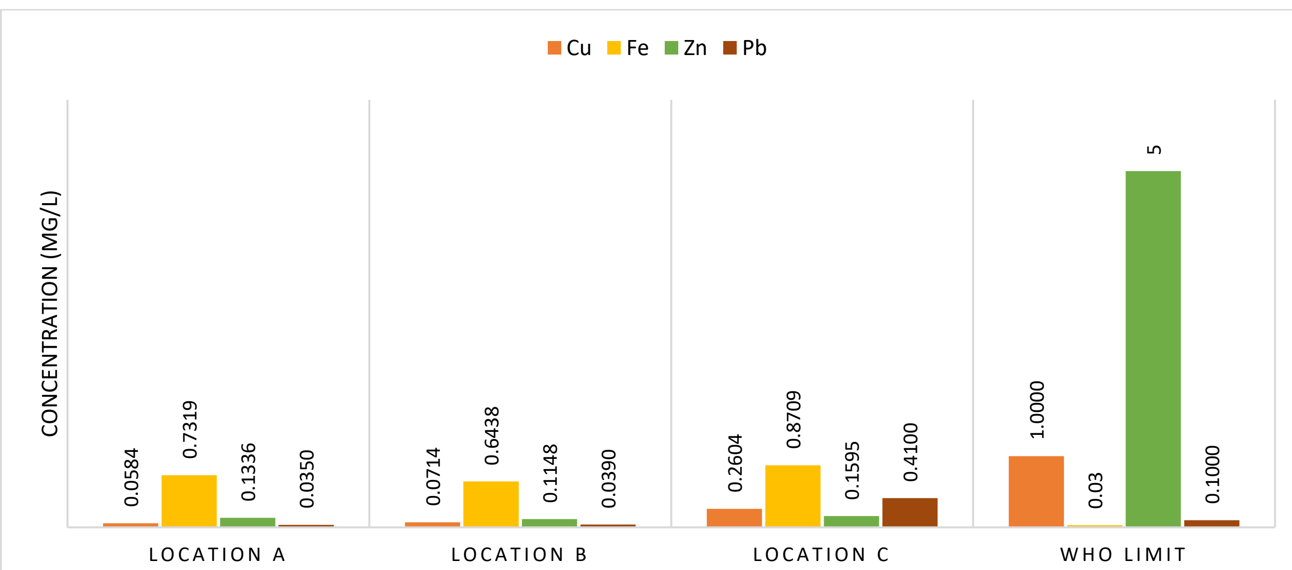


Fig. 2 Bar chart comparing concentrations of heavy metals in cow milk (raw) with WHO permissible limit

As observed from Table II, the mean and standard deviation were displayed for heavy metals in the cow milk (raw) samples got from the study location. From table III, it was observed that location C had the highest average concentration of Copper (Cu) in the cow milk (raw) samples (0.2604 mg/l) followed by those obtained from location B (0.0714 mg/l) and the least concentration was from location C (0.0584 mg/l). The obtained values were within the WHO acceptable limits. The obtained values were lower than the values reported from previous studies in Saudi Arabia and Egypt [5], [1] with the exception of Cu concentration obtained from sample location C (0.2604 mg/l) that was above the obtained values reported by [5], [9] and [6]. [1] linked high concentration of Copper in the blood and tissue to cause kidney, liver and heart damage while acute exposure result in vomiting and bloody diarrhea. The concentration of

Zinc (Zn) indicated that location C had the highest mean concentration of 0.1595 mg/l followed by location A (0.1336) and the least concentration was from location B (0.1148 mg/l). The most elevated mean concentration of Zinc (0.1595 mg/l) in this study was below the reported value as conducted by [6] in Maiduguri, Nigeria. For Iron (Fe), the levels of Iron (Fe) in cow milk (raw) samples obtained from location C was the highest (0.8709 mg/l) followed by those from location A (0.7319 mgl^{-1}) and the least levels was found from the samples obtained from location B (0.6438 mg/l). The highest mean level of Lead (Pb) was found in the cow milk (raw) samples from location C (0.4100 mg/l) followed by samples from location B (0.0390 mgl^{-1}) and the least concentration levels was found from location A (0.0350 mg/l).

The result shows that the Lead (Pb) and Iron (Fe) concentrations in all the raw cow milk samples collected from all the three Local Government areas (Gwale (A), Dala (B) and Ungogo (C)) were all above the WHO permissible limits. Location C was found to have the highest mean concentration of heavy metals in the cow milk (raw) samples (0.4100 mg/l), this could be due to the existence of nearby petrol station in the area, Pb is mainly released from fossil fuels and agricultural pesticides.0.4100 mgl^{-1} lead concentration as reported in this study is below the lead value obtained by [9] in their study.

The higher lead content in the raw milk could also be as a result of possible contaminated water, soils and vegetation that the cattle feed on in the area. Lead is a known carcinogen which is toxic to humans, lead at low level is even harmful [18]. Elevated levels of lead in milk is of increasing concern especially for children and infants who consume the product much, this makes them vulnerable to the harmful effects of carcinogens when exposed to lead. Lead exposure affects the brain and impairs memory amongst the children while cardiovascular effects and elevated high blood pressure occurs in older people.

High concentration of Fe has been reported to affect the kidney, liver and cardiovascular systems. However, the amount of Copper and Zinc levels in all the samples of milk collected from the area adhere to the acceptable limit of WHO. The highest average Zinc concentration in cow milk (raw) samples which was from location C (0.1595 mgl^{-1}) is lower than the values reported by [13] and [9]. Exposure to Zinc in large amount has been reported to cause leucopenia, anaemia, diarrhea and gastrointestinal diseases.

In sample Location A, it was observed that the levels of Iron concentration were very high (0.7319 mgl^{-1}) which then followed by Zinc concentration (0.1336 mgl^{-1}), followed by Copper concentration (0.0584 mgl^{-1}), and the lowest average levels was found in Lead (0.0350 mgl^{-1}).

In sample Location B, it was observed that the levels of Fe concentration were very high (0.6438 mg/l), followed by Zn concentration (0.1148 mg/l), followed by Cu concentration (0.0714 mg/l) and the least concentration was found in Pb (0.0390 mg/l).

In sample Location C, it was observed that the levels of Fe concentration were also very high (0.8709 mg/l), followed by Lead concentration (0.4100 mg/l), followed by concentration of Copper concentration (0.2604 mgl^{-1}) and the lowest concentration was found in Zinc (0.1595 mg/l).

Figure 2 displays the average concentration of heavy metals as compared with WHO limit. It was observed that Lead and Iron contents were above the WHO permissible limits while Zinc and Copper levels in all the cow milk (raw) samples were found to adhere to the WHO acceptable standard limit.

IV. CONCLUSION AND RECOMMENDATIONS

Milk provides the required nutrients to both young and old who consume the product more than ever before, hence it is important to assess the amount of heavy metals present in those milk in order to detect the potential effects of those excessive metals on human health. From the results of this study, it could be concluded that, the levels of Zinc and Copper in cow milk (raw) samples that were obtained from the three selected local governments areas (Gwale local government [Kofar Na'isa Area], Dala local government [Bajallabe Area] and Ungogo local government [Janguza Area] (Sample locations A, B and C respectively) were all below and within the WHO permissible limit. This is an indication that all the milk collected from those locations were all good, safe and fit for human consumption. However, Iron and Lead concentration in the cow milk (raw) samples that were obtained from the study locations were above the recommended limit of WHO. The study hence recommends for routine and further identification of heavy metals in cow milk (raw) samples in other local government, Kano State to ascertain the safe levels of metals in those milk product to the consumers. Farmers should ensure clean and hygienic fodders are given to their cows to reduce lead exposure via feed and water.

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