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Concentrations Of Heavy Metals In Fresh Cow Milk (Nunu) And Nigerian Dwarf Goat Milk In Calabar, Nigeria

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Abstract: ***This study examined the concentrations of Pb, Cd, Cr, Ni, Fe, Cu, Zn, and Co in fresh Cow milk (Nunu) and Nigerian Dwarf Goat milk in Calabar, Nigeria. Samples collected were analysed using Atomic Absorption Spectrophometer (AAS) which was aimed at determining the heavy metal concentration of the above listed metals. The mean concentrations of metals (mg/kg) in the samples are in the ranges of BDL (Below Detectable level) for Cd, 0.07 ± 0.01 for Cu, 0.16 ± 0.01 for Cr, BDL for Co, 0.09 ± 0.01 for Ni, 0.26 ± 0.08 for Fe, 0.02 ± 0.01 for Pb, and 0.16 ± 0.02 for Zn during wet season in cow milk. And BDL for Cd, 0.10 ± 0.01 for Cu, 0.15 ± 0.01 for Cr, BDL for Co, 0.10 ± 0.01 for Ni, 0.16 ± 0.01 for Fe, BDL for Pb and 0.14 ± 0.02 for Zn during wet season in goat milk. In dry season the mean concentrations of metals are in the range of BDL for Cd, 0.10 ± 0.01 for Cu, 0.15 ± 0.01 for Cr, BDL for Co, 0.10 ± 0.01 for Ni, 0.16 ± 0.01 for Fe, 0.02 ± 0.00 for Pb, and 0.17 ± 0.02 for Zn during dry season in cow milk. And BDL for Cd, 0.08 ± 0.01 for Cu, 0.08 ± 0.01 for Cr, BDL for Co, 0.13 ± 0.01 for Ni, 0.16 ± 0.01 for Fe, BDL for Pb and 0.15 ± 0.01 for Zn in goat milk during dry season respectively. Copper and Iron showed significant differences across the seasons P<0.05. The research showed that cadmium and cobalt were below detectable limits; copper was significantly higher in cow milk during the dry season compared to the wet season, while Iron was significantly higher in cow milk during the wet season compared to the dry season. Other metals i.e Ni, Pb, Zn, and Cr did not show any significant difference across the seasons P>0.05. As the concentrations did not exceed the safety limits, they could not pose a serious danger to public health. Hence cow and goat milks can be consumed by humans in Calabar.***

Keywords: Lead(Pb), Cadmium(Cd), Chromium(Cr), Nickel(Ni), Iron(Fe),Copper (Cu), Zinc (Zn), Cobalt (Co), Cow milk(Nunu), Goat milk

I. INTRODUCTION

Heavy metal refers to any metallic chemical element that has a relatively high density and is toxic and poisonous at low concentration or quantity. Examples of heavy metals include Arsenic (As), Lead (Pb), Mercury (Hg), Cadmium (Cd), Chromium (Cr), Thallium (Tl) etc. (Lenntech, 2012). Trace elements are also known as heavy metals e.g. Copper (Cu), Selenium (Se) and Zinc (Zn). They are essential in maintaining the body metabolism, but are toxic at higher concentrations (Lenntech, 2012). The heavy metals can enter bodies through food, drinking water and air (Lenntech, 2012). The heavy metals concerned with the environmental science include; Pb, Cd, Cr, Cu, Zn, Manganese (Mn), Nickel (Ni), Silver (Ag) etc. (Akpan *et al*, 2009). Krajnc *et al*.,(1983) reported that heavy metals in animals can occur through the

ingestion of forage feed and water while in human being, cadmium contamination can occur by the utilization of dairy products like meat and milk. Goat milk is the best substitute for people who cannot digest cow milk or are allergic to cow milk, thus goat milk has significant role in human nutrition, like other foods (Hejtmankova *et al*.,2002). It was found that highly toxic elements like lead and cadmium appeared in both raw and pasteurized goats milk which did not exceed the polish standard (Krelowska-kulas et al.,1999). Miller *et al*.,(1969) found a small fraction of dietary cadmium accumulated in goats milk.

Herbs and vegetables are major sources of nutrients for Ruminants (Cattle, goats etc).There is an inherent tendency of plants to take up toxic substances including heavy metals that are subsequently transferred along the food chain (Singh *et al*., 2010). The main sources of heavy metals to herbs, vegetable and crops are their growth media (soil, air, nutrient solutions) from which these heavy metals are taken up by the roots or foliage (Lokeshwari and Chandrappa, 2006). Vegetables can take up and accumulate heavy metals in quantities high enough to cause clinical problems to humans (Alam *et al.*, 2003). Sabir et al., 2003 reported that due to the grazing of cattle on contaminated soil, higher levels of metals have been found in beef and mutton. Miranda *et al*.,(2005) discovered contaminated animal feed and rearing of livestock in proximity to polluted environment and was reportedly responsible for heavy metal contamination in meat. Prabu,(2009) reported the importance of water resources particularly surface waters in meeting the water need of animals and industries, he indicates the essential need to protect them against contamination.

The aim of this study was to determine the concentrations of heavy metals in fresh cow milk (nunu) and fresh goat milk with an objective of determining the concentrations of some selected heavy metals (Lead(Pb), Cadmium(Cd), Copper(Cu), Chromium(Cr),Nickel (Ni), Iron(Fe), Zinc(Zn) and Cobalt(Co)) present in the samples.

II. MATERIALS AND METHODS

STUDY LOCATION

This study was conducted in Ikot Ekpo cattle and goat market which is situated in the outskirt of Calabar metropolis, Calabar, Cross River State, Nigeria. Calabar is the capital of Cross River State, Nigeria. It lies within Latitude 4° 57 0'N and Longitude 8° 19 30E.

COLLECTION OF SAMPLES

Fresh milk samples from 20 cattle and 20 Nigeria dwarf goats collected from a local cattle and goat market in Ikot Ekpo, Calabar. The fresh animal milk samples were collected in properly washed and cleaned sample bottles with tight fitting screw caps. The bottles were rinsed with milk samples, filled and sealed, in such a way that no air bubbles remained in the bottles. All milk simples were transported to the undergraduate laboratory of the department of pure and applied chemistry, University of Calabar, Calabar for further atomic spectrophotometric analysis. The samples were stored in labeled sample bottles in a Refrigerator at a temperature range between 0°C-4°C (32°F - 40°F) until required for heavy metal analysis.

Preparation of Samples for Analysis. One gram (Ig) of each sample was weighed into a beaker and 15ml perchloric with 10ml of nitric acids added, and heated until the whole sample got digested to a clear solution which was then diluted to a 100ml. The diluted sample was then analyzed in atomic absorption spectrophotometer (AAS) for various metals. The data were analyzed using a t-test statistical method. The result were compared to world Health Organization Standard for milk and student t-test was used to find out if there is any signification difference between the heavy metals in cow milk and goat milk.

III. RESULTS

The result of this research is presented in wet and dry seasons.

HEAVY METAL CONCENTRATION IN COW AND GOAT MILK DURING WET SEASON

The mean concentration of the heavy metals (Pb, Cr, Cd, and Cu) in cow milk for the wet season were recorded at 0.02 ± 0.01, 0.16 ± 0.01, BDL and 0.07 ± 0.01 respectively (Table 1). Also the mean concentration of heavy metal (Fe, Ni, Zn and Co) in cow milk for the wet seasons were 0.26 ± 0.08, 0.09 ± 0.01, 0.16 ± 0.02 and BDL respectively (Table 1).

In the same vein, the mean concentration of heavy metal in Pb, Cr, Cd, Cu, Fe, Ni, Zn and Co in goat milk for the wet season were recorded at BDL (Pb), 0.15 ± 0.01(Cr), BDL (Cd), 0.10 ± 0.01(Cu), 0.16 ± 0.01 (Fe), 0.10 ± 0.01 (Ni), 0.14 ± 0.00 (Zn) and BDL(Co) respectively (Table 1). Their maximum allowable limits were recorded at 0.05 (Pb), 0.03 (Cr), 0.026 (Cd), 0.1 (Cu), NA (Fe), 1 (Ni), 3.28 (Zn), NA (Co) Table 1.

Heavymetal Metal	Mean Concentration mg/kg (mean ± SD)		SD
	CM	GM	WHO (MAL)
Pb	0.02 ± 0.01	BDL	0.05
Cr	0.16 ± 0.01	0.15 ±0.01	0.3
Cd	BDL	BDL	0.026
Cu	0.07 ± 0.01	0.10 ± 0.01	0.1
Fe	0.26 ± 0.08	0.16 ±0.01	NA
Ni	0.09 ± 0.01	0.10 ± 0.01	1
Zn	0.16 ± 0.02	0.14 ± 0.00	3.28
Co	BDL	BDL	NA

CM - Cow Milk, GM - Goat Milk, MAL - Maximum allowable limits,
BDL - Below Detectable Limits, NA - Not Available.

Table 1: Heavy Metal Concentration (mg/kg) in Cow and Goat Milk During Wet Season

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HEAVY METAL CONCENTRATION IN COW MILK AND GOAT MILK DURING DRY SEASON

The mean concentration of heavy metal (Pb, Cr, Cd and Cu) in cow milk during dry season were recorded at 0.02 ± 0.00, 0.15 ± 0.01, BDL, and 0.10 ± 0.01 respectively (Table 2). While the mean concentration of heavy metal in (Fe, Ni, Zn and Co) in cow milk for the dry season was 0.16 ± 0.01, 0.10 ± 0.01, 0.17 ± 0.02 and BDL respectively (Table 2).

In the same vein, Pb, Cr, Cd, Cu, Fe, Ni, Zn and Co in goat milk for the dry season were recorded at BDL, 0.08 ± 0.01, BDL, 0.08 ± 0,01, 0.16 ± 0.01, 0.13 ± 0.02, 0.15 ± 0.01 and BDL respectively (Table 2). Their maximum allowable limits were recorded at 0.05(Pb), 0.3(Cr), 0.026(Cd), 0.1(Cu), NA(Fe), 1.0(Ni), 3.28(Zn) and NA(Co).

Heavy metal	Mean concentration mg/kg (mean ± SD)		
	CM	GM	WHO(MAL)
Pb	0.02 ± 0.00	BDL	0.05
Cr	0.15 ± 0.01	0.08 ± 0.01	0.3
Cd	BDL	BDL	0.026
Cu	0.10 ±0.01	0.08 ± 0.01	0.1
Fe	0.16 ± 0.01	0.16 ± 0.01	NA
Ni	0.10 ± 0.01	0.13 ± 0.02	1.0
Zn	0.17 ± 0.02	0.15 ± 0.01	3.28
Co	BDL	BDL	NA

CM - Cow Milk, GM - Goat Milk, MAL - Maximum allowable limits,
BDL - Below Detectable Limits, NA - Not Available.

Table 2: Heavy Metal Concentration (mg/kg) in Cow and Goat Milk During Dry Season

DISCUSSION OF HEAVY METALS IN COW AND GOAT MILK DURING WET AND DRY SEASONS

Lead(Pb) is well known for its toxic and adverse effects on human. Absorption of ingested Pb may constitute a serious risk to public health. Some chronic effects of Pb poisoning are abdominal pain, constipation and anaemia (Bolger et al; 2000; Uluozlu et al; 2007). Lead was reported in human breast milk (Llobet et al., 2003).The average mean concentration of Pb in the analyzed samples ranged from 0.02 ± 0.01 mg/kg in cow milk and 0.02 – 0.00mg/kg in goat milk. The main source of Pb in foods may possibly come from food handling. The concentration of Pb in the samples analyzed were not above the guideline value for Lead (Pb). Maximum allowable limits from WHO is 0.05mg/kg. Copper is an essential metal and serves as anti-oxidant and help the body to remove free radicals, prevent cell structure damage (Radwan and Salaman,2006) and plays an important role in bone formation and skeletal mineralization (Marian *et al*.,2005). The limit for Cu in food is 10mgkg^{-1} (Europian Commission, 2006).The values of Cu reported in these study were lower than the values reported in the literature for snacks samples (Cabrea *et al*, 2003; Salaman and Radwan,2006;Soylak et al,2006).While that of WHO is 0.1mg/kg. The mean concentrations of Cd in these study appeared to be below detectable limit for both fresh cow milk and goat milk during wet season, and the maximum allowable limits for food is 0.02mg/kg i.e WHO standards. The codex committee of food addictives and contamination draft guideline for Cd in foods is 0.05mgkg^{-1} (CCFAC, 2001; European Commission, 2006). The concentrations of Ni reported in this study were similar to Ni levels found in snacks and appetizer in Turkey (Soylak et al., 2006) and confectioneries (Gopalani et at, 2007), which is below maximum allowable limits (WHO) standard of Ikg/mg. The maximum level of Fe was observed in cow milk while the minimum level is observed in goat milk. Iron has been reported for appetizers and snacks in Turkey (Soylak *et al*., 2006).These food items are potential source of Fe for both children and adults. Deficiency of Fe in the body could result into anaemia, and a maximum allowable limit for (WHO) standard is Not Allowed (NA). The highest mean level of Zn was observed in goat milk while the lowest mean level of Zn was observed in cow milk. The recommended dietary allowance of Zn is 10mg day-1 for growing children and 15 mg day-1 for adult (Saviparumal and others 2007). Zinc deficiency is marked with retarded growth and hypogonadism, leading to decreased fertility. The maximum allowable limit for Zn is 3.28mg/kg. Chromium is an essential trace element and the biological usable form of Cr (Cr3+) potentiates insulin action and, plays a significant role in glucose, lipid and protein metabolism. However, Cr(iv) is carcinogenic (Ikem and Egiebor, 2005, Iwegbue, 2011). It has been estimated that humans require nearly 1 ug day^{-1}.WHO limits as 0.3mg/kg. The mean concentration of Cr in these samples were in the range of 0.01 – 0.16 mgkg^{-1} in cow and 0.01 – 0.15mg/kg. The highest Cr concentration was observed in cow milk while the lowest concentration of Cr was observed in goat milk. The sources of Cr contamination in food are mainly from manufacturing processes and leaching of Cr from the vessel in which these are stored.

Cobalt is a component of Vitamin B12 and has a low oral toxicity. However, excessive intake of a Co could result into cardiomyopathy (Hokin et al., 2004). Normal daily intake is reported to be in the range of 2.5 to 3.0 mg day^{-1}. poisoning occurs within the range greater than 23 - 30 mg Co day-1 (Hokin et al., 2004). The average concentration of Co in this study is below detectable limits and the WHO standard is Not Available. The concentrations of selected metals in fresh milk of cow and goat during dry season are displayed in table II. The JECFA provisional Tolerable Daily intake for Pb is 3.6 µg kg^{-1} bw day^{-1} (WHO, 2000). The average mean concentrations of Pb in the samples analyzed during dry season were 0.02 ± 0.00 mg kg^{-1} for cow milk and BDL for goat milk. WHO standard as 0.05 mg/kg which is below standards. The estimated daily intakes of Ni in this study ranged between 0.10 ± 0.01 mg/kg in cow and 0.13 - 0.02mg/kg in goat. The world Health Organization (WHO) tolerable daily intake (TDI) of Ni is 1mg kg^{-1} bw day^{-1}. Higher dietary intakes of Ni are expected from the consumption of egg roll, hot dogs, sausage oil, puff, chin-chin, bread and spongy cake. Similar intake values of have been reported for confectioneries in India (Dahiya et al., 2005). The dietary intake of Ni does not lead to any health risk in the general population but could be troublesome to some sensitized individuals (Dahiya et al., 2005, Duran et al., 2009).

The estimated intake of Fe from consumption of the product ranged between 10.8 - 71.8 µg Kg^{-1} bw day^{-1}. The

upper tolerable intake of Fe in children (0 months - 8 years) and males/female (14- 70 years) is 40 and 45 mg day-1 respectively. (Institute of Medicine; 2003). The recommended dietary allowance (RDA) of Fe is 10 – 18 mg day-1 person (Demirezen and Drue, 2006). The estimated intake of Fe in this study constitutes 0.5% of the recommended dietary allowance for Fe. The concentration in the study ranges from 0.01 – 0.16 mg kg^{-1} in cow and 0.01 – 0.16mg/kg in goat while the WHO acceptable limit is Not Available. The joint Expert Committee on Food Addictives (JECFA) provisional Maximal Tolerable Daily Intake (PMTDI) for Zn is 1000 µg kg^{-1} bw day^{-1} (WHO, 1982). The Expert Group on vitamins and Minerals (EVM) Safe Upper Level (SUL) is 42 mg day^{-1} (equivalent to 700 µg kg^{-1} bw day^{-1} in a 60kg adult) for total dietary intake (EVM, 2003). The estimated dietary intakes of Zn in this study are in the range of 0.02 -0.17 mg kg^{-1} bw day-1 in cow and 0.01- 0.15 mg/kg in goat which is equivalent to 1.6 - 3.8% of the EVM Safe Upper Level. And Maximum allowable limits as 3.28mg - 4.3 µg kg^{-1} bw day^{-1} through the consumption of any of these food types. The mean concentration of Cu in the analyzed samples appears in 0.10 ± 0.01 mg kg-1 in cow milk and 0.08 - 0.01 in goat milk. The recommended maximum allowable limit for Cu is 0.1mg/kg.

The vast majority for Cr found in food is in the trivalent form (Anderson, 1994). To prevent deficiency, the Committee on Medical Aspect of food policy (COMA) has recommended that Cr should be above 0.25mg day^{-1} for adult and 1.0 - 1.0µgkg^{-1} bw day^{-1} for children and adolescents respectively (Ministry of Agriculture, Fisheries and Food (MAFF) 1999). The estimated dietary intakes of Cr from these foods constituted 0.15 - 0.01 mg kg"1 in cow and 0.08 – 0.01mg/kg in goat milk and the allowable limits as 0.3mg/kg.

The recommended dietary allowance (RDA) value for Co is 100µg/day (Nutrition Data 2000, .Amidzic Klaric et al, 2011). The estimated intake of Co in this sample analyzed is BDL which makes it lower than the recommended dietary allowance. And maximum allowable limit from (WHO) Not Available. Cow milk was examined for heavy metal contents across seasons to determine if there will be significant differences in heavy metal concentration per season. From the results, Cadmium and Cobalt were below detectable limits; copper was significantly higher in cow milk during the dry season. Compared to the wet season, Iron was significantly higher in cow milk during the wet season compared to the dry season. Other metals i.e Ni, Pb, Zn, and Cr did not show any significant difference across the seasons ($P > 0.05$)

Goat milk was also examined for heavy metal contents across seasons to determine if season played a significant role in metal levels. From the results, Cd, and Pb were below detectable limits while no significant difference ($p>0.05$) was observed across seasons for other detected metals.

IV. SUMMARY AND CONCLUSION

In conclusion, the heavy metals such as Cd, Co in cow milk and Pb in goat milk were not detected during wet season even though they were reported in milk in several studies. The heavy metals; (Pb in cow milk Cr, Cu, Fe, Ni and Zn) were detected in milk samples gotten from the study area.

In dry season, heavy metals such as (Cd, Co in cow milk and Pb in goat milk) were not detected, while other metals detected are (Pb in cow milk, Cr, Cu, Fe, Ni and Zn for both goat and cow milk respectively. The concentrations of heavy metals observed were comparable with some of the reported value in literature. The results obtained for detected elements in the present study were also compared with international daily intake guideline of different international organizations such as (WHO/FAO) for food and were found to be below the levels allowed.

During the wet season goat milk showed values of Cu that was close to the maximum allowable limits, while other metals were significantly below maximum allowable limits. During the dry season cow milk showed Cu concentrations that were close to the maximum allowable limits while other metals were significantly below maximum allowed limits.

In summary, change in seasons was observed to have no significant effect on the heavy metal concentrations of cow milk and goat milk in Ikot Ekpo cattle and goat market in Calabar, Nigeria.

In conclusion, metal values in milk during a particular season that were close to the maximum allowable limits may indicate potential risk for consumer populations.

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