Chemistry Research Journal, **2020, 5(6):71-78**

Available online www.chemrj.org

Research Article

ISSN: 2455-8990
CODEN(USA): CRJHA5

Quantitative Analysis of Selected Heavy Metals in Samples of Branded and Unbranded Cow Milk in Selected Areas of Kaduna Metropolis

I. Sani[1], B El-yaqub[1], SO Okeniyi[1], AB Shehu[2]

[1]Department of Chemistry, Faculty of Science, Nigerian Defence Academy, Kaduna, Nigeria
[2]Food Technology and Home Economics Department, NAERLS/ABU Zaria, Kaduna, Nigeria

Abstract Twenty four (24) samples of unbranded cow milk and fifteen (15) various brands of branded co w milk (BCM) were used in this study. Atomic absorption spectrophotometric method using wet digestion analytical method was made use of to determine the concentration of Pb, Cr, and Cd in the samples. The results indicates that the main concentration of Cd, Pb and Cr were 0.0014ppm, 0.0017ppm and 0.0028 for UCM and 0.0017ppm, 0.0015ppm and 0.0015ppm for BCM respectively. The concentration of the heavy metals were within limit stipulated by WHO and the Nigerian industrial standards (NIS) with the exception of one sample were Cd level was above limit.

Keywords Heavy metals, Wet digestion, cow milk, Atomic absorption spectrophotometric

Introduction

Milk is a food of outstanding interest and has been taken by humans since the earliest pre-historic times and still forms the basis of most nation economies [1]. Milk is considered to be a complete food for young animals and of high nutritional value to humans. The constituents of milk include, protein, fat, total solid, lactose, etc. Also, milk contains hundreds of minor constituents which include milk fat, vitamins, metal ion and flavor compounds [2]. Animals are reared to produce milk for consumption by humans, although, cow is by far the most important in commercial terms [3] and White Fulani (Bunaji) as native breed in west Africa was recognized as the principal producer [4].

Trace metals are a general collective term applying to the group of metals and metalloids with an atomic density greater than 6 g/cm. This term is widely recognized and usually applied to the elements such as cadmium (Cd), Cu, Fe, lead (Pb), and Zn which are commonly associated with pollution and toxicity problems [5]. One of the main problems with metals is their ability to bio-accumulate. Metal residues in milk are of particular concern because milk is largely consumed by infants and children [6]. The food chain is an important source of Cd and Pb accumulation, especially for plants grown on polluted soils. Significant amounts of Cd and Pb can be transferred from contaminated soil to plants and grass, causing accumulation of these potentially toxic metals in grazing ruminants, particularly in cattle [7]. Accumulation of Cd and Pb in ruminants causes toxic effects in cattle, but also in humans consuming meat and milk contaminated with toxic metals [8]. Cd and Pb are amongst the elements that have caused the most concern in terms of adverse effects on human health. This is because they are readily transferred through food chains and are not known to serve any essential biological function. Lead is a pervasive and widely distributed environmental pollutant with no beneficial biological roles. The poisoning is more common in farm ruminants, which are considered most susceptible to the toxic effects of lead [9].

Material and Methods

Sample Collection and Preparation

Polyethylene sampling bottles were soaked in 20% HNO_3 for 24 hours and rinsed with deionized water before collection of raw milk in order to avoid possible contamination. Sampling was carried out across various milk markets in Kaduna metropolis, three replicate samples were collected at each sampled area which included Railway market, Rido, Kasuwar Barchi, Zango Cattle Market, Kajuru, Panteka, Kasuwar Magani and Kaduna Central Market. Branded Cow Milk. (BCM) were purchased across the counter at various supermarket in Kaduna metropolis. Each of the brand was purchased three times at different time interval and each with different batch number [10]. The name of each Sample was replaced with an alphabet from A- Z for unbranded and A-O for branded. Names were followed by U meaning the product is Unbranded, or B meaning that the product is branded.

Sample Digestion

Each sample ($1cm^3$) was digested with $5cm^3$ of concentrated hydrochloric acid (HCl) and $5cm^3$ of concentrated perchloric acid ($HClO_4$), all analytical grades. The digested samples were quantitatively transferred into $50cm^3$ flask, made up to the mark with distilled water and stored in $50cm^3$propylene bottles. This was digested by heating the content in the beaker to nearly dryness. After evaporation and cooling, $20cm^3$ of distilled water was added to the beaker, stirred and filtered into $50cm^3$ volumetric flask and filled to the mark with distilled water. It was then transferred into $50cm^3$ sample bottle, the digested sample was allowed to cool at room temperature. A specified amount of distilled water was added into the digested residue and filtered through what man filter paper No 1. The volume of the filtrate was made up to 100ml using distilled water and the solution was further diluted before determinations of lead (Pb), Chromium (Cr) and Cadmium (Cd) using Flame Atomic Absorption Spectroscopy (FAAS). The digestion was carried out in triplicate for the blank, standard and samples. Digestion of a reagent blank was also performed in parallel with milk samples keeping all digestion parameters the same for heavy metals determination [11].

Results and Discussion

Lead Concentrations in BCM and UCM

As indicated by data in table 1 and 2, the mean concentrations of lead was in the range of 0.0009 – 0.0014 ppm with the highest mean concentration from brand 5 and lowest from brand 1 of the BCM and the elemental concentrations of BCM and UCM are presented in Fig 1 and 2. The highest mean concentration of lead in UCM was recorded in the samples from Panteka (0.003133 ppm). The lowest concentration of was recorded in the samples from Kasuwar Magani (0.001633 ppm). The mean concentrations of lead in this study were lower than those reported by Ogabiela *et al.,* [11] in the assessment of metal levels in Challawa Industrial area of Kano state and Zaria, Tasse *et al.,* [12] determination of concentrations of selected heavy metals in cow's milk: borena zone, Ethiopia and Bilandžić *et al.,* (2011) in the northern and southern Croatia, Mahmud *et al.,* [13] recorded lead below detection level in cow milk samples at Kawo, Kudenda and above the permissible limit at Malali in Kaduna, , while high levels of lead were reported in Egypt. The levels of lead in milk samples from both UCM and BCM were within the acceptable limit of lead for milk and dairy product taken as 0.02 ppm as stipulated by Nigerian Industrial Standard on Cow Milk.

This study suggest that lead is detected in milk in most of the studied BCM and UCM samples particularly those areas where metals are fabricated and processed like Panteka, lead is also detected in other unsuspecting brands and areas like Rido, Kasuwar Barchi and Kajuru. These are areas where little or no industrial activity exist however, This could be due to fodder contamination, climatic factors such as wind, use of Agro-chemicals and very importantly drinking water. Furthermore, these cows graze along rail lines, roadsides etc. lead which is a fuel additive could be emitted from the car exhaust to contaminate the environment [11].

Lead is one of the limited classes of element that can be described as purely toxic. Most other elements thought toxic at high concentration are actually required nutrient at lower levels. There is no exposure level below which lead appears to be safe. High level of lead is particularly of great concern especially due to the fact that milk and dairy products are consumed mostly by infants and children who are uniquely susceptible to the effect of lead [11]. Lead absorption constitutes serious risk to public health. It induces reduced cognitive development and intellectual performance in children, increased blood pressure, and cardiovascular diseases in adult as well as liver and kidney malfunctioning [11].

Table 1: Lead Metal Concentration (ppm) from BCM

Sample	Brand 1	Brand 2	Brand 3	Brand 4	Brand 5
1	0.0009	0.0014	0.0022	0.002	0.0012
2	0.0008	0.0012	0.0016	0.0022	0.0014
3	0.001	0.002	0.0012	0.0016	0.0016
Mean	0.0009	0.001533	0.001667	0.001933	0.0014
±	±	±	±	±	±
Std	0.0001	0.000416	0.000503	0.000306	0.0002

Table 2: Lead Metal Concentrations (ppm) from UCM

Sample Location	Panteka	Railway Market	Rido	Kasuwar barchi	Zango cattle market	Kajuru	Abubakar Gummi Market	Kasuwar Magani
1	0.004	0.0016	0.0026	0.0002	0.0032	0.0021	0.0036	0.003
2	0.003	0.0006	0.0024	0.0006	0.0024	0.0014	0.0026	0.001
3	0.0024ii	0.0021	0.0021	0.0014	0.0021	0.0018	0.002	0.0009
Mean	0.003133	0.001433	0.002367	0.000733	0.002567	0.001767	0.002733	0.001633
±	±	±	±	±	±	±	±	±
Std	0.000808	0.000764	0.000252	0.000611	0.000569	0.000351	0.000808	0.001185

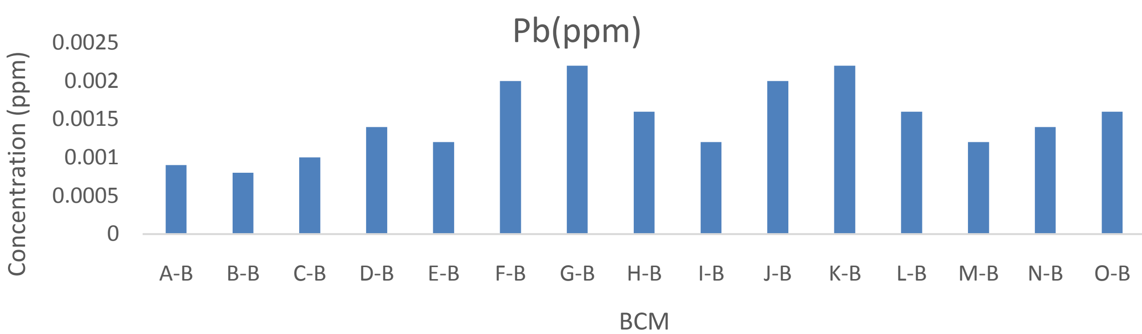

Figure 1: Elemental concentrations (ppm) of Pb in BCM

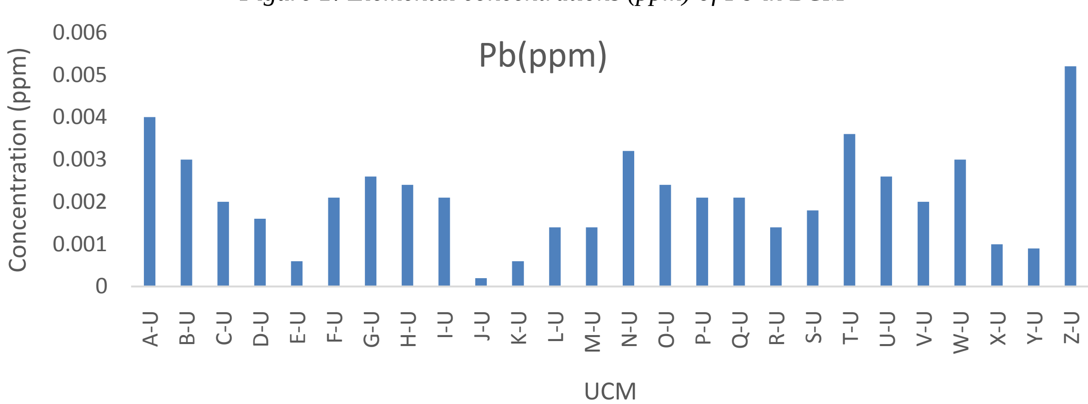

Figure 2: Elemental concentrations (ppm) of Pb in UCM

Cadmium Concentrations in BCM and UCM

The mean concentrations of cadmium obtained in this research ranges from 0.0007 -0.003267 ppm for BCM and 0.00013 -0.0032 ppm for UCM the values obtained where all within the limit of 0.2 ppm as specified by the Nigerian Industrial Standards for cow milk, Fig 3 and 4 shows elemental concentrations of Cadmium in BCM and UCM, it is also within the limit of the recommended dietary allowance given as 0.5 mg/day [13]. Similar levels was reported by Hasan and Arzu [14] in Samsung region of Turkey. Renata *et al.*, [15] recorded lower levels of lead and Cadmium in Simmental cow milk, however higher values were reported by Mahmud *et al.*, [13] in the analysis of selected heavy metals in cow milk in kudenda, Malali and Kawo areas of Kaduna state. This suggests that the environment, air and the feeds the animal ingest is not contaminated with cadmium. However bio accumulation may occur with continues ingestion of small amount of cadmium as the metal is not biodegradable. Sample X-U of Kasuwar Magani was found to be at unsafe levels (fig 3), this may be attributable to anthropogenic activities via industrial discharges, emissions and inorganic fertilizer that may pollute the environment, air and water bodies which indirectly or directly get to the fodder of the animals [11]. A high levels of Cd in cow milk was reported by Ogabiela *et al.*, [11], Blandzic *et al.*, [16], Abdulkhaliq *et al.*, [17] and Tassew *et al*., [12].

Regular absorption of cadmium causes damage to the proximal renal tubules and calcium, phosphorus, glucose, amino acid and small peptides are loss in the urine. Once cadmium accumulates in tissues it cannot be removed safely by chelation therapy without causing kidney damage [13]. Cadmium affects calcium metabolism and skeletal changes resulting from calcium loss and ends in a decrease bone mineral density [13].

Table 3: Cadmium Metal Concentration (ppm) from BCM

Sample	Brand 1	Brand 2	Brand 3	Brand 4	Brand 5
1	0.0009	0.001	0.0013	0.007	0.0014
2	0.0007	0.0019	0.0018	0.0009	0.0011
3	0.0005	0.0015	0.0016	0.0019	0.0012
Mean	0.0007	0.001467	0.001567	0.003267	0.001233
±	±	±	±	±	±
Std	0.0002	0.000451	0.000252	0.003272	0.000153

Table 4: Cadmium Metal Concentration (ppm) from UCM

Sample	Panteka	Railway Market	Rido	Kasuwar Barchi	Zango Cattle Market	Kajuru	Abubakar Gummi Market	Kasuwar Magani
1	0.001	0.0009	0.0017	0.0005	0.0017	0.0014	0.0018	0.0019
2	0.0019	0.007	0.0011	0.0013	0.0 017	0.0016	0.0019	0.0009
3	0.0009	0.0017	0.0012	0.00017	0.0015	0.0019	0.0022	0.0055
MEAN	0.001267	0.0032	0.001333	0.000657	0.0016	0.001633	0.001967	0.002767
±	±	±	±	±	±	±	±	±
Std	0.000551	0.003315	0.000321	0.000581	0.000141	0.000252	0.000208	0.002419

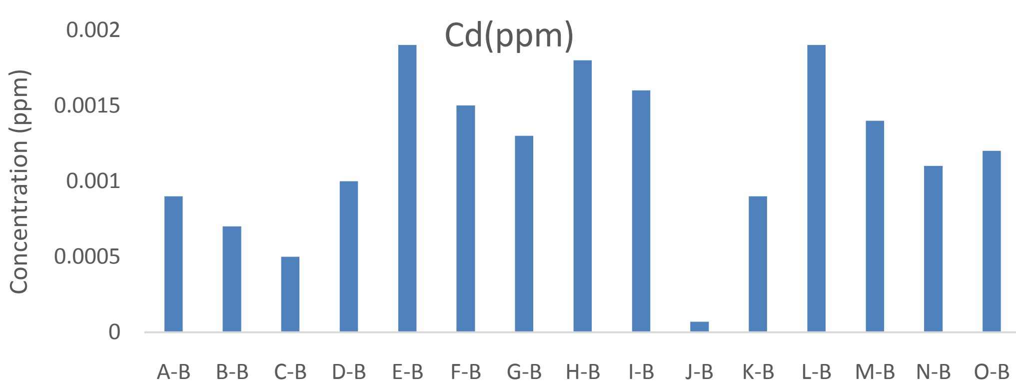

Figure 3: Elemental concentrations (ppm) of Cd in BCM

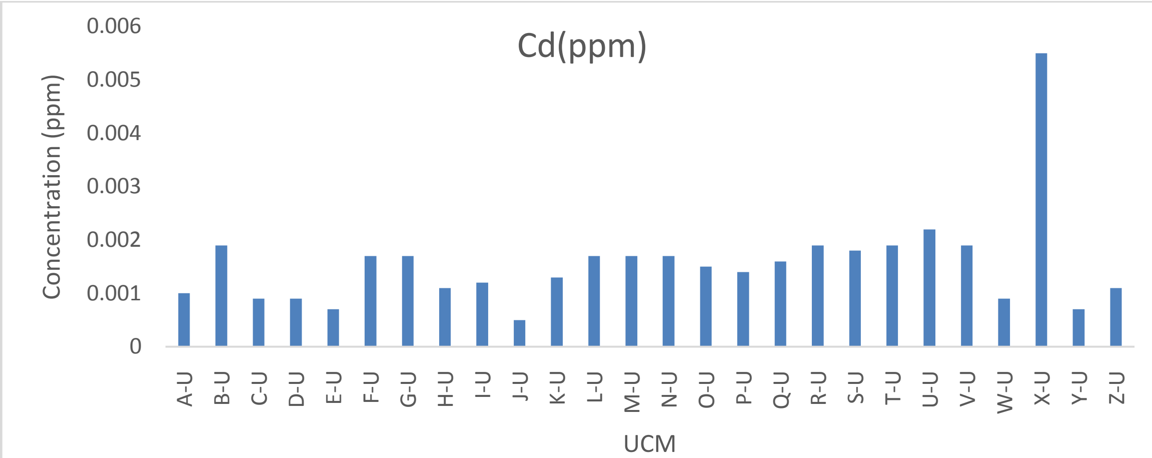

Figure 4: Elemental distribution of Cd (ppm) in UCM

Chromium concentrations from BCM and UCM

The average levels of Cr in milk samples analyzed from UCM and BCM from the investigation is shown in table 1.5 as 0.0028 ppm and 0.0015 ppm respectively. The highest concentration recorded was 0.002367 ppm and the lowest concentration 0.000533 ppm for the various brands of BCM considered. While the concentrations recorded for UCM is in the range of 0.000933 – 0.0032 ppm, Mahmud *et al.*, [13] found chromium below detection limit in the determination of heavy metals in cow milk in selected areas in Kaduna metropolis. Higher concentrations were recorded by Ogbabiela *et al.*, [11] in Kano, Tassew *et al.*, [12] in Ethopia.

Chromium is a useful mineral in the body found in the blood and hair, it aids in proper functioning of insulin and blood cholesterols. There is no data available for the maximum limit of chromium in milk [12]. However, daily intake of chromium intake of 50- 200μg/day is acceptable by WHO. Lower availability of chromium in the body can lead to skin irritation, and ulceration. However excessive amount of Cr in the body can cause kidney and liver failure, circulatory and nerve tissue problems [18].

Table 5: Chromium Metal Concentration of BCM

Sample	Brand 1	Brand 2	Brand 3	Brand 4	Brand 5
1	0.0004	0.0017	0.0008	0.0014	0.0012
2	0.0006	0.0028	0.0012	0.0012	0.0011
3	0.0006	0.0026	0.0014	0.0024	0.001
Mean	0.000533	0.002367	0.001133	0.001667	0.0011
±	±	±	±	±	±
Std	0.000115	0.000586	0.000306	0.000643	1E-04

Table 6: Chromium Metal Concentration of UCM

Sample	Panteka	Railway Market	Rido	Kasuwarbarchi	Zango cattle market	Kajuru	Abubakar Gummi Market	Kasuwar Magani
1	0.0018	0.0018	0.0017	0.0026	0.0028	0.0017	0.003	0.0017
2	0.0006	0.0016	0.0016	0.0028	0.0024	0.0016	0.0022	0.0062
3	0.0004	0.003	0.0084	0.0009	0.0038	0.0023	0.0044	0.0058
Mean	0.000933	0.002133	0.0039	0.0021	0.003	0.001867	0.0032	0.004567
±	±	±	±	±	±	±	±	±
Stdev	0.000757	0.000757	0.003897	0.001044	0.000721	0.000379	0.001114	0.002491

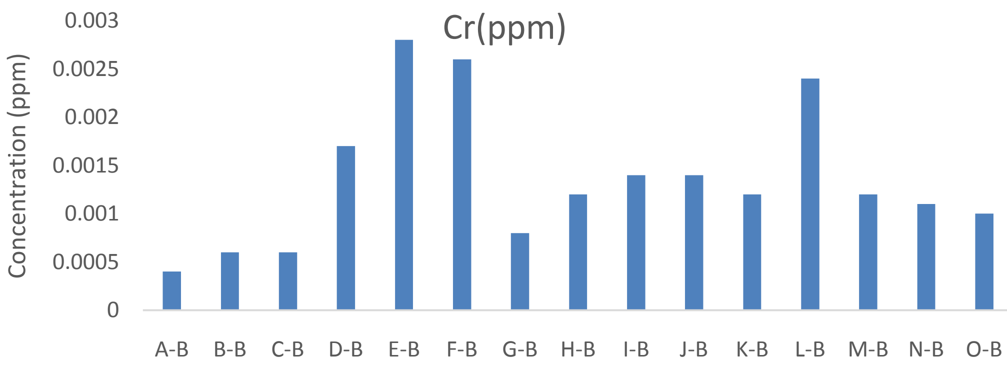

Figure 5: Elemental concentrations (ppm) of Cr in BCM

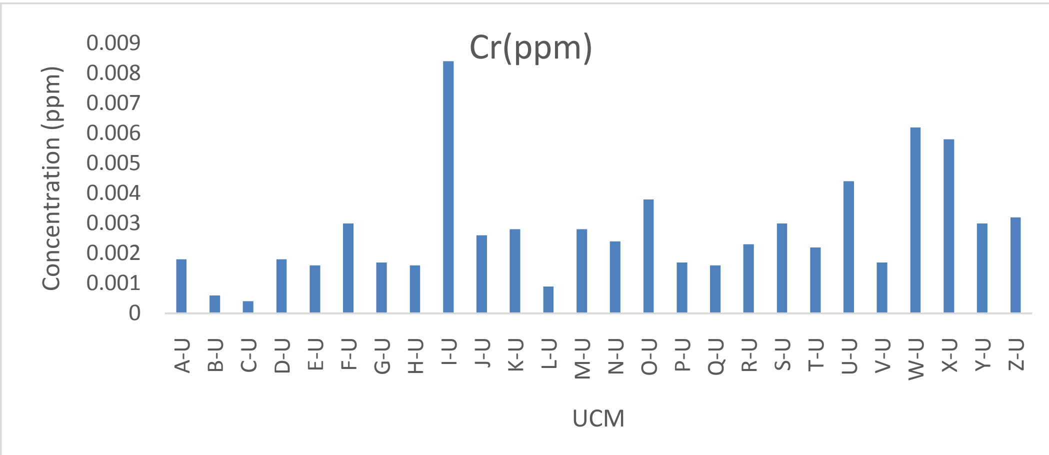

Figure 6: Elemental distribution of Cr (ppm) in UCM

Comparison of Pb, Cd and Cd in BCM and UCM

The UCM has higher concentration of lead cadmium and chromium as shown in the elemental distribution in fig. 7 and 8. This could be due to fodder contamination, climatic factors such as wind, use of Agro-chemicals and very importantly drinking water [11]. Furthermore, these cows graze along rail lines, roadsides etc. lead which is a fuel additive could be emitted from the car exhaust to contaminate the environment [11].

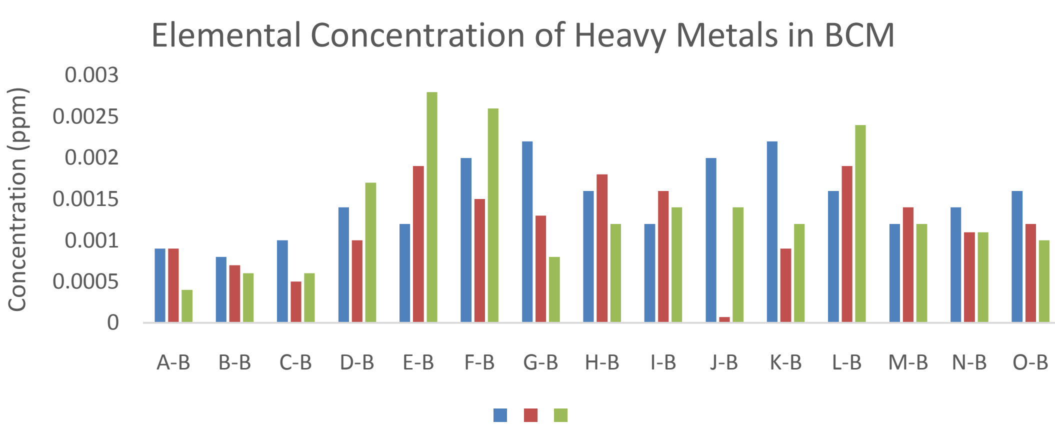

Figure 7: Comparison of concentrations (ppm) of heavy metals of all BCM samples

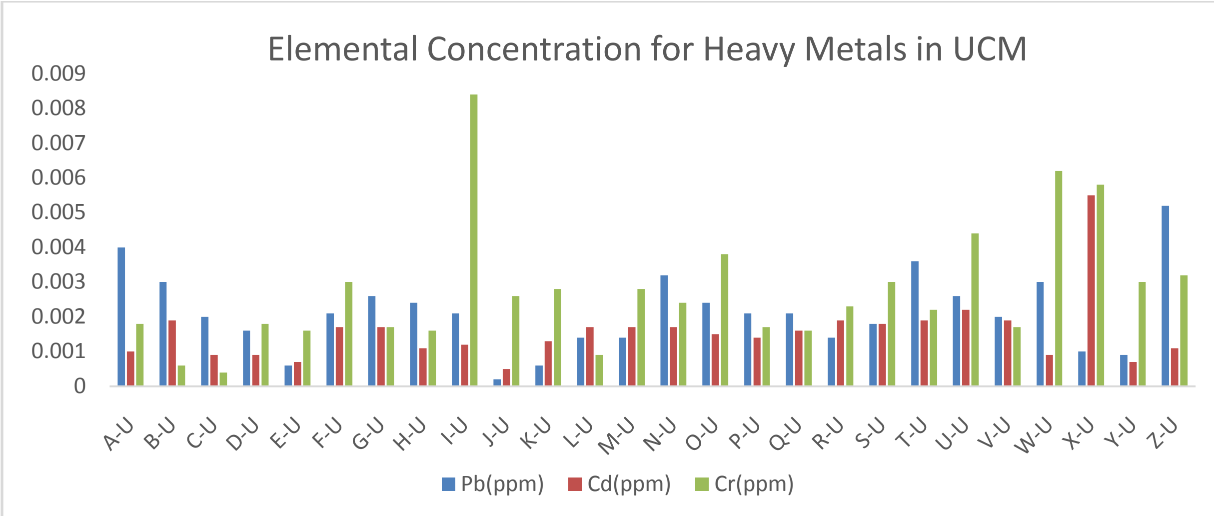

Figure 8: Comparison of concentrations (ppm) of Pb, Cd and Cr in UCM

Conclusion

In this present study, the concentration of Cr, Cd and Pb were analyzed in cow milk samples collected from different markets within Kaduna metropolis. The results revealed that the levels of Lead, Cadmium and Chromium in the studied BCM and UCM samples collected within Kaduna metropolis were found to be within the limit specified by the Nigerian Industrial Standards on cow milk, WHO and the recommended dietary allowance except for cadmium metal in one of the UCM samples. The results also show the consumption of Chromium via all samples was much higher than that of Lead and Cadmium.

References

[1]. Alfa, L. (1987). Dairy Handbook. (2) New Age International Publisher Limited, London, pp 23 -27.

[2]. Armstrong, H.C. (1995). Food and nutrition (3) New Age International Publisher Limited, London pp 69 – 70.

[3]. Adams, M.J. and Moss M.O. (1995). Food Microbiology. New Age International Publisher Limited, New Delhi. pp 64 – 66.

[4]. Adeneye, J. A. (1989). Variations in yield and composition of milk from different quarters of lactating White Fulani cattle in a tropical environment. *Nigerian Journal of Animal Production*, 16: 8-15.

[5]. Malhat, F., Hagag, M., Saber, A., and Fayz, A.E. (2012). Contamination of Cows milk by heavy metal in Egypt. *Bulletin of Environmental Contamination and Toxicology*. 88(4):611–613.

[6]. Tripathi, R. M., Raghunath, R., Sastry, V. N. and Krishnamurthy T. M. (1999). Daily intake of heavy metals by infants through milk and milk products. *Science of the Total Environment*. 1999; 227(2–3):229–235. doi: 10.1016/S0048-9697(99)00018-2. Vromman V.

[7]. Lopez, C. E. L., Ramos, L. L., Ramadan, S. S. and Bulacio, L. C., (2003). Presence of aflatoxinM_1 in milk for human consumption in Argentina. *Food Control: 14*, (31-34).

[8]. González-Walez, J. R., Senís, E., Gutiérrez, A.and Prieto, F. (2012). Cadmium and lead in bovine milk in the mining area of the Caudal River (Spain) *Environmental Monitoring and Assessment*, 184(7):4029–4034. doi: 10.1007/s10661-011-2241-1.

[9]. Swarup, D., Patra, R. C., Naresh, R., Kumar, P. and Shekhar, P. (2005). Blood lead levels in lactating cows reared around polluted localities; transfer of lead into milk. *Science of the Total Environment*. 347(1–3):106–110. doi: 10.1016/*j.scitotenv*.2004.12.055.

[10]. Farid, S. M., Enani, M. A. and Wajid, S. A., (2004). Determination of trace elements in cow's milk in Saudi Arabia., *JKAU Engineering Science.*, 15(2), 131-140.

[11]. Ogabiela, E.E, Udiba, U.U, Adesina, O.B, Hammuel, C., Ade-Ajayi, F., A., Yebpella, G.G., Mmereole, U.J. and Abdullahi, M. (2010). Assessments of metals levels in fresh milk from cows grazed around Challawa Industrial Estate Kano, *Journal of Basic and Applied Science Resource.* 1(7):533-538 2011.

[12]. Tassew, B,Ahmed, H. and Vegi M. (2015). Determination of Concentrations of Selected Heavy Metals in Cow's Milk: Borena Zone, Ethiopia. *Journal of Health Science* 2014, 4(5): 105-112 DOI: 10.5923/j.health.20140405.01

[13]. Mahmud, M. I., Muhammad, Z. and Zakari A. (2017). Determination of Some Heavy Metals in Milk of Cow Grazing At Selected Areas, of Kaduna Metropolis. *International Journal of Advanced Research in Computer Science and Software Engineering a* (716)/01617, 341-346.

[14]. Hasan, T. and Arzu S. (2012). Heavy metal concentrations in raw milk collected from different regions of Samsun, Turkey. *International Journal of Dairy Technology* 65 (4):516-522.

[15]. Renata, P. Jerzy, W., Paweł, C., Piotr, S., Bogumiła, P. and Agnieszka (2013). Concentrations of toxic heavy metals and trace elements in raw milk of Simmental and Holstein-Friesian cows from organic farm. *National Center for Biotechnology Information* (NCBI). 185(10): 8383–8392.

[16]. Bilandžić, N., Dokić, M., Sedak, M., Božica, S., Varenina, I. and Knežević, Z. (2011). Trace element levels in rawmilk from northern and southern regions of Croatia. *Food Chemistry.* 127(1) *63*–66. doi: 10.1016/j. 2010.12.084.

[17]. Abdulkhaliq, A., Swaileh, K. M., Hussein, R. M. and Matani, M. (2012). Levels of metals (Cd, Pb, Cu and Fe) in cow's milk, dairy products and hen's eggs from the West Bank, Palestine, *International Food Resource Journal*, 19(4) 1039 -1047.

[18]. Lenntech, (2004). Water Treatment and Purification, Lenntech, Rotterdamseweg, Netherland. 54 – 60.