

Levels of Some Heavy Metals in Fresh Cow Milk obtained from Herder settlement around Okada, Benin City, Edo State Nigeria.

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Abstract: The study focused on profiles of heavy metals in Cow Milk compared with corresponding values of different researchers in Nigeria and other countries. Fresh Cow Milk samples (obtained from a herder settlement outside Okada town, Benin City, Edo State in Nigeria) were carefully collected from lactating cows digested and subjected to heavy metal analysis using atomic absorption spectroscopy. All the metals (Fe, Pb, Cu, Cd, Co, Mn, Zn and Ni) assessed were found to be present in all the samples. The analyzed metal profiles are as follows: concentration of Fe, Cu Zn Pb Cd, Co, Ni and Mn ranged from 0.586 to 0.652, 0.287 to 0.384, 0.129 to 0.232, 0.022 to 0.036, 0.005 to 0.019, 0.046 to 0.082, 0.070 to 0.086, 0.073 to 0.087 mg/l respectively. Iron, lead, nickel and cadmium contents in this study did exceed the tolerance limits of WHO/SON Standards, giving rise for concern of the consumption of fresh milk (obtained from this area) and its uses to produce related consumable products.

Keywords: Heavy metals, Fresh cow's milk, atomic absorption spectroscopy

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I. Introduction

Metals have been classified as essential, beneficial, or detrimental. Trace elements recognized as essential for human health include iron, copper, zinc, cobalt, chromium, iodine, molybdenum, and selenium (Sarkar, 2002). The second group of elements thought to be beneficial to life are silicon, nickel, boron, manganese, and vanadium. Detrimental metals or metals that are regarded as purely toxic metals such as lead, mercury and cadmium are not known to provide any essential or potentially beneficial health effect at any level of exposure (Sarkar, 2002).

Heavy metals are persistent contaminants in the environment that can cause serious environmental and health hazards. They are among the most dangerous contaminants in the environment and are released into the environment from natural as well as an anthropogenic activity, although many of them, under suitable conditions, play a role in key bio-chemical reactions necessary for correct functioning of the human body. These metals are co-factors in many enzymes and play an important role in many physiological functions of man and animals (Koh and Judson, 1986; Ogabiela *et al.*, 2010).

Heavy metals, even though they occur in small amounts, are a serious threat to the human organism, causing e.g. anaemia, dementia, neurological changes, psychic disturbances, inhibition of enzyme activity, disturbances in the absorption of iron, damage to the kidneys, muscular atrophy, as well as cancers of the mouth, lungs, genital glands (Sujka, *et al.*, 2019). Although metals are essential nutrients, having a variety of biochemical functions in all living organisms and important industrial uses, these metals even in low concentrations are however potentially toxic to humans and animals.

Milk is an important source of all basic nutrients required by mammals including human beings. Milk from various mammals such as cow, goat, buffalo or sheep is used for different nutritional purposes, e.g. feeding to young ones and preparation of some nutritional products such as milk cream, yogurt, butter, sour milk, etc. (Hassan, 2005; Ogabiela *et al.*, 2010). Studies on products of animal origin (e.g. milk) indicate a considerable variation in the concentration of Cd, Hg, Pb and other heavy metals, from trace levels to amounts exceeding the maximum allowable concentrations many times (Kabata-Pendias, 1999; Sujka, *et al.*, 2019)

Lactating cows may be exposed to high quantities of toxic metals in the environment by air, water and through grazing on grass/feeds from polluted fields or near roads with heavy traffic. Dairy animals may ingest metals while grazing on the pasture. However, in the cow, transfer of minerals to milk is highly variable. Milk being the fundamental content in infant and child feeding and the basic raw material for the production of many food products, its content of heavy metals should be monitored as a matter of priority (Sujka *et al.*, 2019).

The concentrations of dangerous metals in the environment grows with increase of urban, agricultural and industrial emissions. Environmental quality and human activities (soil, water, river, industry, mining, and smelting) play a key role in the distribution of toxic metals in raw milk and contribute to Pb, As, and Cd contamination in animals and transfer to milk (Robert *et al.*, 2020). Metals have been reported by Nigerian researchers in a variety of foodstuffs in the country, it is therefore necessary to monitor and control their levels in consumed food. The aim of the present study is to quantify the concentration of heavy metals namely Fe, Ni, Cu, Cd, Zn, Mn, Co and Pb in fresh cow's milk collected from grazing settlement in the outskirts of Okada town, Edo State, Benin City; the observed mean elemental concentrations (i) compared with the WHO/FAO permissible limits, (ii) regressed against reported values of other researchers in other countries and (iii) determine the hazards or otherwise of the use of fresh cow milk for consumption and production of related products.

II. Materials And Methods

Sample Collection

Raw milk samples from lactating cows grazed in a herder settlement in the outskirts of Okada town were collected in February 2021. The milking was done by nomads in the morning milking directly into sterile screw bottles. They were preserved in coolers packed with ice blocks and transported immediately to the laboratory at Igbinedion university, Okada and then placed in refrigerator to avoid fermentation prior to digestion.

Sample Digestion

Milk of 10 mL concentration was digested with 1:3 of H₂O₂ and HNO₃. The samples were heated on hot plate until their volume reduces to 2 mL. The digested samples were filtered and transferred into 50mls flask, made up to the mark with distilled water and stored in 50mls propylene bottles at 4°C until analysis. The samples were later analyzed by Atomic Absorption Spectrophotometer.

Elemental Analysis

Metal concentration in the digest was determined by Atomic Absorption Spectrophotometer (AAS) with background correction. The flame condition and graphite furnace were optimized for maximum absorbance and linear response with the aspiration of known standard. The heavy metals selected for study were Fe, Ni, Cu, Cd, Zn, Mn, Co and Pb. The standards were prepared from 1000 ppm stock solution, in each case of the selected metals, three different concentrations were made to calibrate the Flame AAS. The resultant calibration curve of well-prepared standard concentrations gives linear curve by Atomic Absorption Spectrophotometric Analysis.

III. Results And Discussion

The results of elemental concentration and average concentration of samples of fresh milk from cows grazed at the outskirts of Okada town are presented in Tables 1 and 2 respectfully. Table 3 represents Heavy Metals concentrations obtained compared with the maximum permissible Limits (MPL) values of WHO and SON

Table 1: Elemental concentration in fresh cow's milk from Okada, Edo State, Nigeria (mg/L)

Samples	Fe	Cu	Zn	Pb	Cd	Co	Ni	Mn
1	0.628	0.348	0.183	0.023	0.006	0.046	0.074	0.086
2	0.598	0.373	0.213	0.036	0.005	0.063	0.083	0.081
3	0.614	0.362	0.194	0.029	0.006	0.082	0.070	0.087
4	0.652	0.384	0.143	0.027	0.008	0.074	0.086	0.085
5	0.592	0.382	0.129	0.025	0.011	0.07	0.080	0.083
6	0.603	0.296	0.232	0.032	0.007	0.068	0.078	0.083
7	0.618	0.287	0.147	0.026	0.008	0.070	0.075	0.073
8	0.586	0.312	0.162	0.022	0.009	0.059	0.080	0.084

Table 2: Statistical analysis of elemental concentration in fresh cow milk in Okada town, Edo State, Nigeria.

Samples	Fe	Cu	Zn	Pb	Cd	Co	Ni	Mn
Mean	0.611	0.343	0.175	0.028	0.008	0.067	0.078	0.083
SD	0.022	0.039	0.036	0.005	0.019	0.011	-0.005	0.004
Max	0.652	0.384	0.232	0.036	0.019	0.082	0.086	0.087
Min	0.586	0.287	0.129	0.022	0.005	0.046	0.070	0.073

The conducted analyses revealed the presence of the analyzed heavy metals in all the milk samples. Basic variation statistical values (arithmetic mean, standard deviation, maximum and minimum value) were determined.

Table 3: Heavy Metals conc. obtained compared with the MPL values of WHO and SON

Metal	Fe	Cu	Zn	Pb	Cd	Co	Ni	Mn
Mean Conc. (mg/l)	0.611	0.343	0.175	0.028	0.008	0.067	0.078	0.083
WHO (mg/l)	0.030	1.000	5.000	0.010	0.003	-	0.030	-
SON (mg/l)	0.030	1.000	5.000	0.010	0.003	-	-	-

MPL – Maximum Permitted Levels

Iron was detected in all the milk samples analyzed, the Fe values of the raw milk samples studied varied between 0.586–0.611 mg/kg (Table 1) with a average concentration of 0.611 mg/L although higher than the WHO standard, when compared to other works, the average concentration of iron obtained in this study is lower than those reported by Patra *et al* (2008), Li-Qiang *et al* (2009), Ghosia *et al* (2014), Serdal *et al* (2016) and Ahmed *et al* (2017) as shown in Fig 1.

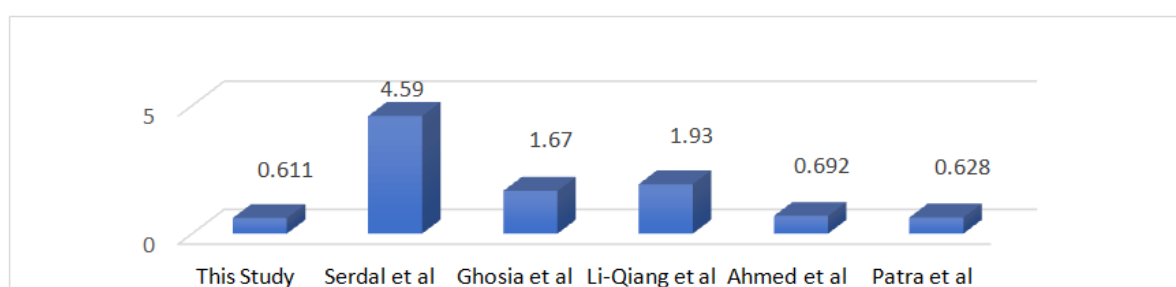


Fig 1: Average concentration of Fe observed compared to other studies.

Copper was detected in all the milk samples with concentrations ranging from 0.287 mg/l to 0.384 mg/l with a mean concentration of 0.343 mg/l. When compared to earlier works the concentration average of copper observed was lower than those observed by Serdal *et al* and Ghosia *et al* but higher than those obtained by Patra *et al* (2008), Qiang *et al* (2009), Ogabiela *et al* (2011), Abdalla *et al* (2013), Ghosia *et al* (2014), Li- Ahmad *et al* (2017) and as shown in Fig 2.

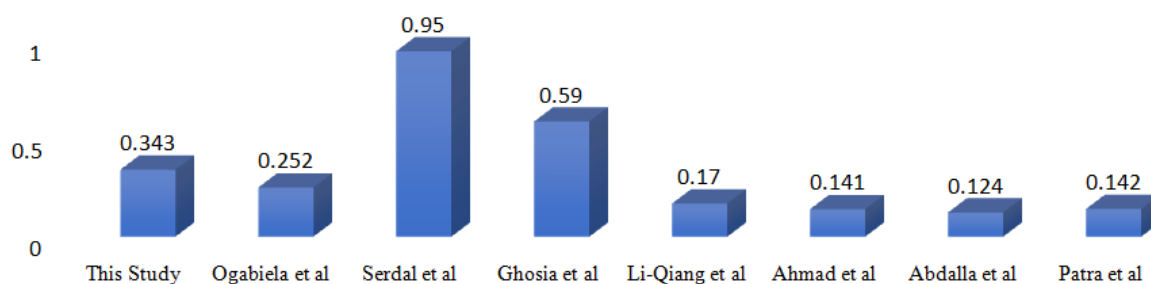


Fig 2: Average concentration of Cu observed compared to other studies

The observed concentration of copper was below the WHO limit stipulated for milk. Copper is an essential element, despite being as inherently toxic as non-essential heavy metals exemplified by lead, plants and animals rapidly accumulate it and is known to cause brain damage in mammals. (Fatoki *et al.*, 2002).

Zinc was detected in all the samples investigated, with concentrations ranging from 0.129 mg/l to 0.232 mg/l and an average concentration of 0.175 mg/l.

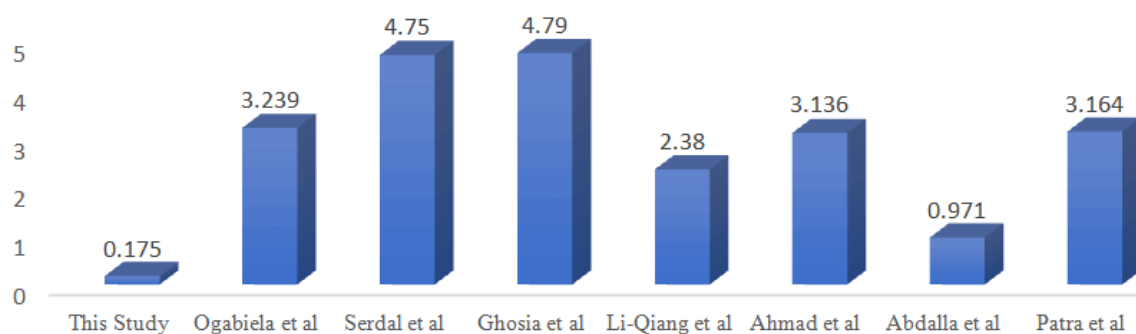


Fig 3: Average concentration of Zn observed compared to other studies

The average concentration of zinc obtained in this study is lower than those reported by Patra *et al* (2008), Li-Qiang *et al* (2009), Ogabiela *et al* (2011), Abdalla *et al* (2013), Ghosia *et al* (2014), Serdal *et al* (2016) and Ahmad *et al* (2017). Zinc, an essential trace element is more toxic in salt form than in elemental form (Lanre-Iyanda and Adekunle, 2012). Happily, zinc does not accumulate with continued exposure; rather, body content is modulated by homeostatic mechanisms that act mainly on absorption and liver levels (Walshe *et al.*, 1994; Asonye *et al*, 2007).

The concentration of lead detected ranged from 0.022 mg/l to 0.036 mg/l. The average concentration of lead obtained in the study is lower than those reported by Patra *et al* (2008), Ogabiela *et al* (2011), Abdalla *et al* (2013), and Serdal *et al* (2016) but higher than that observed by Ghosia *et al* (2014) and in-line with the result reported by Li-Qiang *et al* (2009).



Fig 4: Average concentration of Pb observed compared to other studies

Lead, a detrimental and purely toxic metal is not known to provide any essential or potentially beneficial health effect at any level of exposure (Sarkar, 2002). Acute lead poisoning result in the following symptoms: headache, irritability, abdominal pain and various symptoms related to the nervous system and in severe cases lead to acute psychosis, confusion and reduced consciousness (Järup, 2003).

The concentrations of Cadmium detected range from 0.005 mg/l to 0.019 mg/l. compared to other studies the average concentration of 0.008 mg/l obtained is higher than those observed by Li- Qiang *et al* (2009) and Abdalla *et al* (2013) but lower than those reported by Patra *et al* (2008), Ogabiela *et al* (2011), Ghosia *et al* (2014), and Ahmad *et al* (2017). as shown in fig. 5.

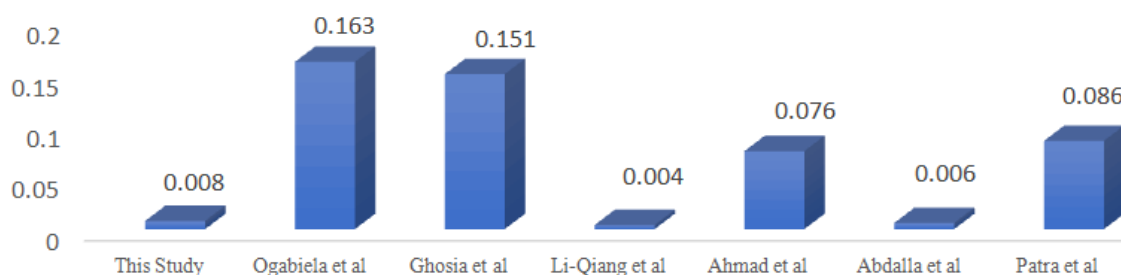


Fig 5: Average concentration of Cd observed compared to other studies

Cadmium a detrimental metal is purely toxic and not known to provide any essential or beneficial effect to human health (Sarkar, 2002). Cadmium exposures are associated with kidney and bone damage, cadmium has also been identified as a potential human carcinogen, causing lung cancer (WHO, 2007).

Cobalt was detected in all the samples, with values ranging from 0.042 mg/l to 0.084 mg/l. The average concentration of 0.067 mg/l observed is higher than the result reported by Abdalla *et al* (2013).

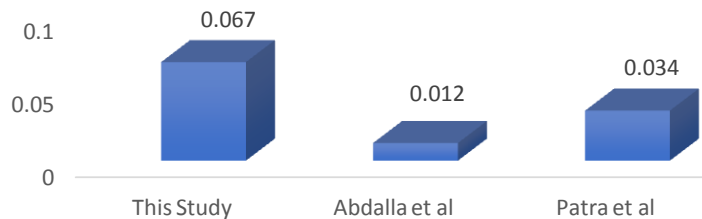


Fig 6: Average concentration of Co observed compared to other studies

Cobalt toxicity in animals' results in gastroenteritis, vomiting and diarrhea occur followed by damage to the liver and kidneys (Meridian, 1991; Agbugui and Nwaedozi, 2015).

Nickel was detected in all the sample with an average concentration of 0.078 mg/l, compared to other works this is higher than the result reported by Patra *et al* (2008), Ghosia *et al* (2014) and Ahmad *et al* (2017) but lower than the result observed by Ogabiella *et al* (2011).

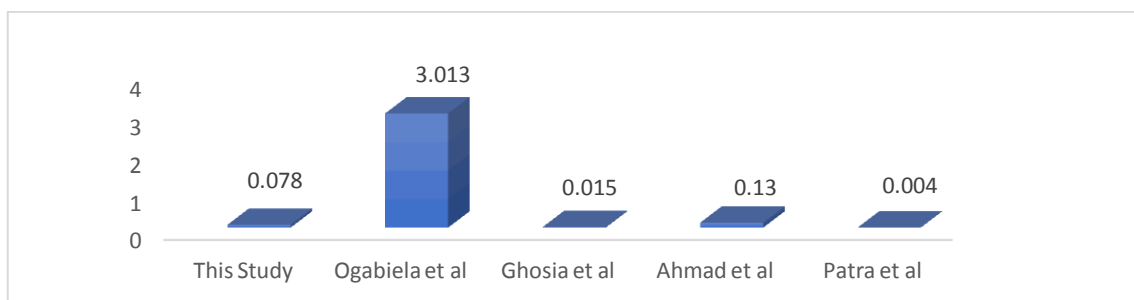


Fig 7: Average concentration of Ni observed compared to other studies.

Nickel an essential element is thought to be beneficial to life, the lungs and nasal cavity are the primary targets for nickel-induced cancers (Sakar, 2002).

The concentration of Manganese detected in the milk sample ranged from 0.073 mg/l to 0.087 mg/l. The average concentration of Manganese detected (0.083 mg/l) was found to be higher than the results reported by Patra *et al* (2008), Li-Qiang *et al* (2009), Ghosia *et al* (2014), and Ahmad *et al* (2017) but lower than the result reported by Ogabiella *et al* (2011).

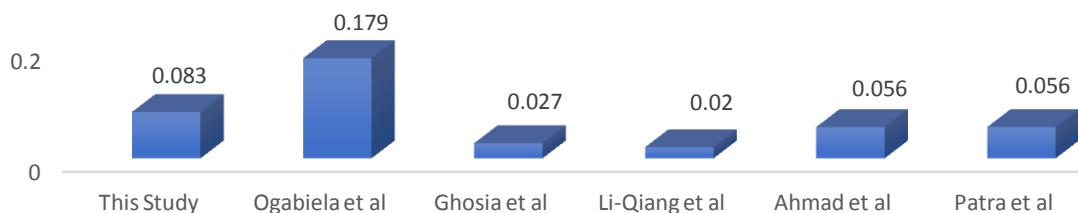


Fig 8: Average concentration of Mn observed compared to other studies

Manganese though beneficial to human health, Toxicity from Manganese manifests with profound increase in the incidence of respiratory diseases, if there is chronic Manganese toxicity, it results to Parkinson-like syndrome (Asonye *et al.*, 2007).

IV. Conclusion

The present study gives important information on the levels of toxic metals (lead and cadmium), beneficial elements (nickel and manganese) and trace elements (zinc, copper, cobalt, and iron) in fresh cow milk. In generally, the average concentrations of the heavy metals detected in fresh cow milk used in this study decreased in the order of Fe > Cu > Zn > Mn > Ni > Co > Pb > Cd. All the heavy metals investigated were found to be present in all the milk samples, though the concentrations fall within the WHO/SON recommended values for fresh milk except iron, lead, nickel and cadmium had average concentrations above the WHO/SON recommended values. Although Iron is an essential metal, its adverse effects which is usually common as frequent acute and chronic iron (Fe) over-load may result to health impairment (Asonye *et al.*, 2007). Cadmium is one of the most toxic heavy metals (Dana, 2014; Onibon *et al.*, 2019); 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. In human body, Cadmium causes renal damage and dysfunction due to accumulates in liver and kidney. Although Lead is poorly absorbed by mammals (Casey *et al.*, 1995), Cardiovascular, hematological and neurological problems occur in exposure to even low quantities (Onigbon *et al.*, 2019). Bioaccumulation of the essential iron, toxic metal cadmium and lead through the food chain and intake from other food stuff should also be of concern. Special attention should be given to these heavy metals as once they are present in concentrations greater than the acceptable limit, it may become difficult to reduce them to an acceptable level during processing.

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