PRINT ISSN 1119-8362
Electronic ISSN 1119-8362

Full-text Available Online at
https://www.ajol.info/index.php/jasem
https://www.bioline.org.br/ja

J. Appl. Sci. Environ. Manage.
Vol. 26 (2) 307-314 February 2022

Evaluation of Public-Health Risk of Heavy Metals Contaminants and Physicochemical Parameters in Adulteration Palm Oil Commonly Consumed in Calabar, Nigeria

(EKPO, GI; ETENG, OE; UKEME, E; EKWU, M; BASSEY, S; UBOH, F

Department of Biochemistry, Faculty of Basic Medical Sciences, University of Calabar, Calabar, Nigeria
**Department of Biochemistry, College of Bioscience, Federal University of Agriculture, Abeokuta, Nigeria*
**Corresponding Author Email: ofemeffiom@gmail.com*

ABSTRACT: Edible palm oil has been the parity of the human diet from generation to generation and has contributed both to nutrition and health. These studies investigated some selected heavy metals and physicochemical parameters in palm oil. Eleven (11) samples of ready-consumed edible palm oil were bought randomly from the selected market in calabar metropolis. The samples were digested with 25ml of concentrated H_2SO4, for heavy metals analysis using Atomic Absorption Spectrophotometer (AAS). The physiochemical parameters in selected markets include the following FFA, IV, PV, and protein content were also analyzed using standard methods. The results showed that FFA value range from 9.26 to 12%, Iodine value range from 45.78 to 21.40 MgKOH/g, Peroxide value range from 3.60 to 0.03 Meq/kg, and protein content ranges from 0.06 to 0.2 mg were significantly ($p<0.05$) higher in some markets in comparison to the control. The results of heavy metals showed that Zn 8.06±0.06, Cd 1.01±0.05, N 1.00±0.00, C 125.91±0.09, Pb 9.30±0.07 Cobalt, Lead zinc were above the detectable limit of the WHO standard while Cd and Ni were within the permissibility limit. The results obtained from this study indicate that the palm oil sold in calabar metropolis may cause a public health risk if proper monitoring is not maintained by regulatory agencies. Thus, there is a need for improved screening of our local processed palm oil from the time of production to the time of consumption.

DOI: https://dx.doi.org/10.4314/jasem.v26i2.19

Impact factor: http://sjifactor.com/passport.php?id=21082

Google Analytics: https://www.ajol.info/stats/bdf07303d34706088ffffbc8a92c9c1491b12470

Keywords: Cadmium, Cobalt, Nickel, Free fatty acids

The highly significant oil-producing plant in West Africa is palm oil (Elaeis guineensis) Otu (2013). The fifth greatest palm oil-producing country is Nigeria Izah *et al.*, (2014) that accounts for approximately 55% of palm oil used in Nigeria and the 45% shortage is supplied by importation from main producing countries including Indonesia and Malaysia. Ohimain and Isiah (2015). Two different kinds of oil are produced by oil palm fruit, which are: brownish yellow crude palm kernel oil extracted from the seeds (kernel) and orange-red crude palm oil extracted from the mesocarp. Palm oil is full of healthy minor ingredients including tocols and carbohydrates (carotenoids and squalene). Crude palm oil includes nearly 400–1000 ppm carotenoids (pro-vitamin A); however, the amount of carotenoids is decreased to a non-detectable level after physical refining Ghazani and Marangoni (2016). The characteristic deep orange-red color is because of carotenoids (500-700 ppm) Gunstone (2005) and its semi-solid consistency at room temperature is basically as a result of the existence of triacylglycerol of palmitic and oleic acids Gee (2007). Palm oil is utilized as a component in producing soap, soap candle, bases for lipstick, margarine, waxes, and polish bases, tin plating, lubricant, pharmaceutical products confectionaries, and in the preparation of some traditional medicine Basiron and weng (2014). As a result, palm oil is a fundamental component of diet to different families in Nigeria Undiandeye and Otarak (2017). Trace elements are of significant benefit to man when consumed in the right proportion, the deficiency of these elements in diet may constitute health problems that may be devastating The presence of trace metals such as copper (Cu), iron (Fe), magnesium (Mg), cobalt (Co), cadmium (Cd), manganese (Mn), and calcium (Ca) in palm oil are known to enhance the amount of oil oxidation while other components like

**Corresponding Author Email: ofemeffiom@gmail.com*

lead (Pb), chromium (Cr), and Cd at certain levels are toxic and they are known to induce multiple organ damage even at lower levels of exposure. Other types of environmental pollutants are heavy metals that can be bio-accumulated by the plant from the contaminated environment Amasha *et al.,* (2020). In addition, they can be leached from the processing equipment by time passage based on the metalloid utilized in the production at the processing facilities. Some groups of heavy metals are essential and needed in trace concentration. The effects of toxicity because of usual heavy metals that pollute the environment and food resources have been documented Izah and Srivastava (2015). Unfortunately, as a result of microbial infestation, palm oil is exposed to deterioration. As stated by Okpokwasili and Molokwu (1996), microorganisms result in chemical alterations that cause deterioration in palm oil quality Kaku and Adenyi (1976). They further mentioned that the incidence of fungi in palm oil is unfavorable and causes the lipolyzation of the oil with the resultant enhancement in Free Fatty Acids (FFA) of the oil. Therefore, the existences of these organisms negatively affect the quality of palm oil by contributing to an enhanced FFA in palm oil together with the fact that the fungi and impurities pose potential health risk to palm oil consumers. Hence, the objective of this paper was to evaluate the public-health risk of heavy metals contaminants and physicochemical parameters in adulterated palm oil commonly consumed in Calabar, Nigeria.

MATERIALS AND METHODS

Study Area: The study was carried out in the Calabar metropolis. Samples were collected from ten markets namely: Marian market, watt, Akim, Mbukpa, Ikot ishie, 8miles, Ekpo Abasi, Guddie, Uwanse, Ikot Effa, and control palm oil at ugep etc.

Geographical Area of Calabar: According to the statistical services in Calabar, it occupies a total land surface of 406 km^2 with a population of 371, 0022.

Sampling of Palm Oil: A total of eleven (11) palm oil samples were collected from ten vendors and one (1) sample of the palm oil was collected from the control area. The samples were collected in sample bottles and stored under ambient temperature. Table below shows the various markets where samples of palm oil were collected.

Sample Digestion: Each sample of the palm oil weighing accurately 1.0 g was digested in a fume cup board by dissolving in 25 ml of concentrated H_2SO4 in separate beakers and then heated to get it all dissolved.

Name of Market	Location	Number of Sample collected
Watt Market	Watt	1
Marian Market	Marian	1
Akim Market	Akim	1
Mbukpa Market	Mbukpa	1
Ikot Ishie Market	Ikot Ishie	1
8miles Market	8miles	1
Ekpo Abasi Market	Ekpo Abasi	1
Guddie Market	Guddie	1
Uwanse Market	Uwanse	1
Ikot Efa Market	Ikot Efa	1
Control palm oil Ugep	Ugep	1

Determination of Heavy Metals: The dissolved palm oil samples were added slowly to 50 ml of distilled water in a 100 ml volumetric flask. The hollow cathode and deuterium lamp were lit, the monochromator was positioned at the required wavelength for the element. The burner head was adjusted to assure that the center of the light beam passes over the burner slot. The flame was lit and the flow of fuel and oxidant were adjusted to make an oxidizing flame (lean blue). De-ionized water was aspirated and the burner head and hollow cathode were warmed for 20 minutes. Calibration blank was aspirated and a zero point was established. A calibration curve was constructed for the standard solution. The unknown samples were aspirated and quality control standards were also aspirated to check for drift. The samples were determined using Atomic Absorption Spectroscopy (AAS), the method by American Public Health Association (APHA).

Determination of the Free Fatty Acids of the Palm Oil: 2 ml of 1% phenolphthalein solution was added to 20 ml of ethanol: diethyl ether (1:1 v/v) mixture and it was neutralized by 0.10 M NaOH solution. After that, 5 g of each oil sample was added to the neutralized mixture and titrates against 0.10 M NaOH solution with constant shaking until a pink color created and remained for 15 minutes. The titer values were used to obtain the free fatty acid value (Admasu and Chandravanshi, 1984).

Iodine Value Determination: 5 ml of Dam's reagent was added to 5 ml of the chloroform solution of the oil. The mixture was Held in a fume cupboard for 10 min and 5 ml of 10% KI and 20 ml of water were added.

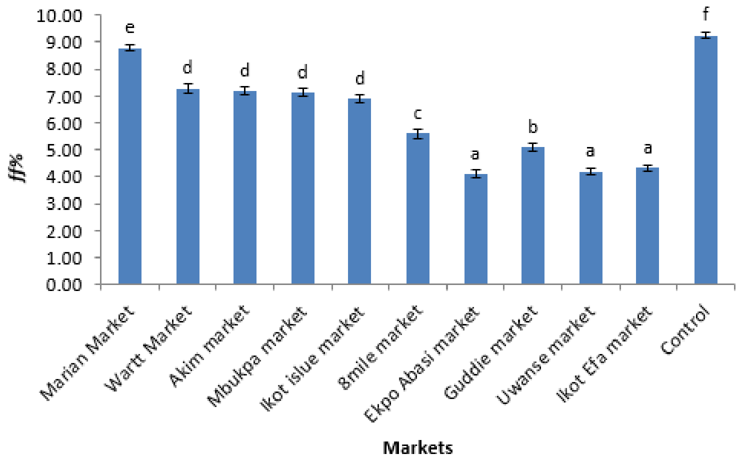

Fig 1. Showing the composition of free fatty acid in all the selected markets

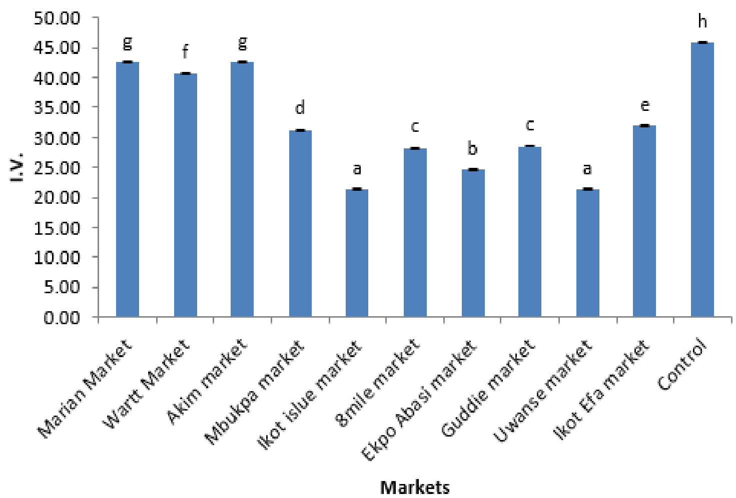

Fig 2 showing the composition of iodine value in palm oil in all the selected markets

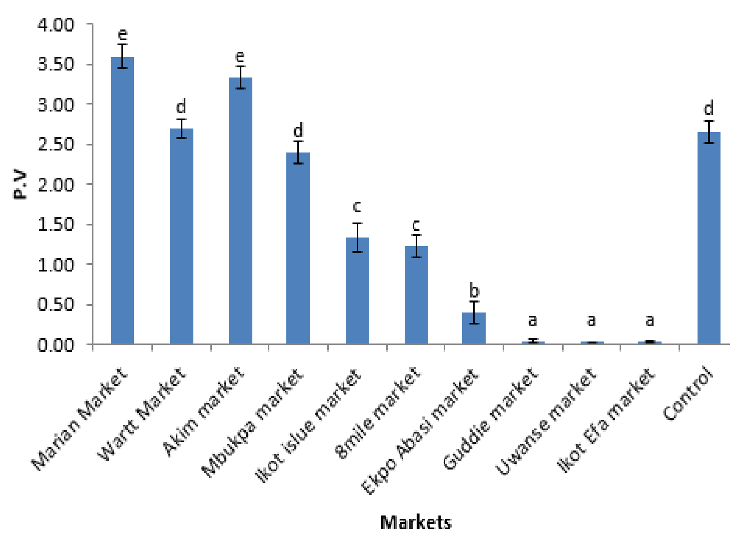

Fig 3 showing the composition of peroxide value in palm oil in all the selected markets

The mixture was completely mixed and titrated to a colorless endpoint with 0.025 M Na 2S2O3. Solution. The control was handled likewise (Baily, 1951).

Peroxide Value Determination: Precisely 1.0 g of KI and 20 ml of solvent mixture (glacial acetic acid: chloroform, 2:1 v/v) were Added to 1.0 g of the oil sample and the mixture were boiled for one minute. The hot solution was poured into a flask containing 20 ml of 5% KIO3 solution. Few drops of the starch solution were dded to the mixture and the latter was titrated with 0.025 M Na 2S2O3 solution

Crude Protein Determination: The Kjeldahl process explained by Pearson was utilized to determine the crude protein content of the oil samples. This method included the determination of total nitrogen which was converted to protein.

Statistical Analysis: The collected data was analyzed using Statistical Package for Social Sciences (SPSS) program version 20. Data were expressed as Mean ± Standard Error of Mean (SEM). Differences between groups were compared by one-way analysis of variance (ANOVA) with $p<0.05$ considered statistically significant.

RESULTS AND DISCUSSION

The results in **figure 1** free fatty acid composition in all the ten selected markets show that there was a significant increase ($p< 0.05$) in the control market in comparison to other markets. There was no significant difference in all the selected markets compared to the control market, respectively. The free fatty acid obtained in the present research range between 4.12-9.26 %. The results in **figure 2** iodine value composition on the palm oil selected in calabar metropolis show a significant increase ($P<0.05$) in four of the markets compared to the control markets while others show no significances (P>0.05) when compared to the control markets, respectively.

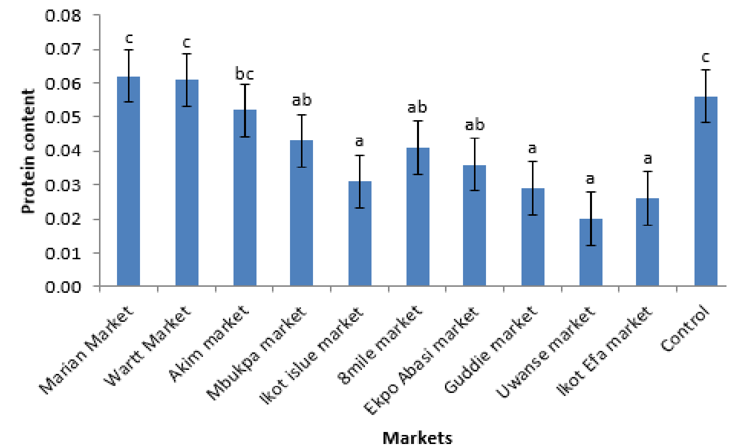

Fig 4 showing the protein content in the palm oil in all the selected markets

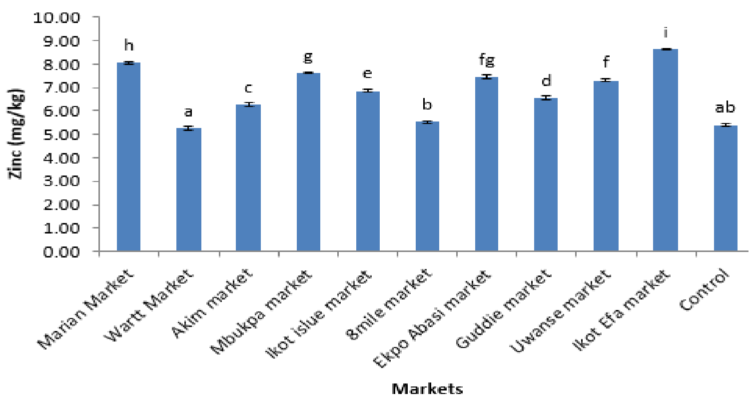

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Fig 5 heavy metal composition (Zinc) of palm oil sold in Calabar metropolis

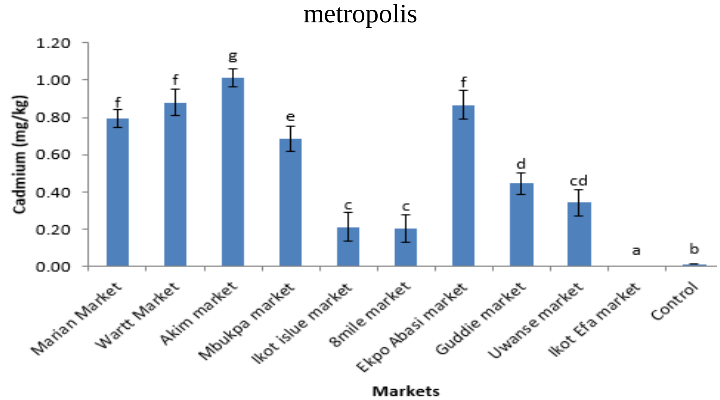

Fig 6 heavy metal composition (Cadmium) of palm oil sold in Calabar metropolis

Hence, the iodine value obtained in this particular study range between 21.4-45.78 %. The results in **figure 3** peroxide value show a significant increase (P<0.05) in almost four of the selected markets in comparison to the control markets. In addition, there was no significant decrease (P>0.05) in some of the market selected markets when compared with the control markets respectively. Moreover, the peroxide value range between 0.03- 3.60 MEq/K which is compared with the standard value of 10 MEq/Kg.

The results in **figure 4** protein content shows a significant difference (P<0.05) in almost all the selected markets sample in comparison to the control market. However, a significant decrease existed in some selected markets when compared to the control markets, respectively. The protein content ranges between 0.06-0.02 Mg/KOH/g.

The corresponding results were obtained with the absorbance against the concentration calibrated for each heavy metal showed in the first table 1. The results in figure 5 show that there was a significant increase P<0.05 across the markets sample in Calabar metropolis, but out of the market sample five markets were significantly higher compared with the control market, respectively. The results in **figure 6** showed the heavy meal concentration of cadmium in palm oil sold in calabar, metropolis. The results further indicated that a significant increase of P<0.05 existed in Akim market and other three markets compared with the control market, respectively. The results in **figure 7** show the concentration of Nickel in palm oil; these results indicate that a significant increase P<0.05 existed in the Uwanse market in comparison to the control market, respectively. The results show the concentration of cobalt in **figure 8** there was a significant increase P<0.05 in Ekpo Abasi market with a random increase across all the entire market in calabar metropolis compared with the control, respectively. The results in **figure 9** show the concentration of Lead. There was a significant increase P<0.05 in Ekpo Abasi market followed with Uwanse market compared with the control, respectively.

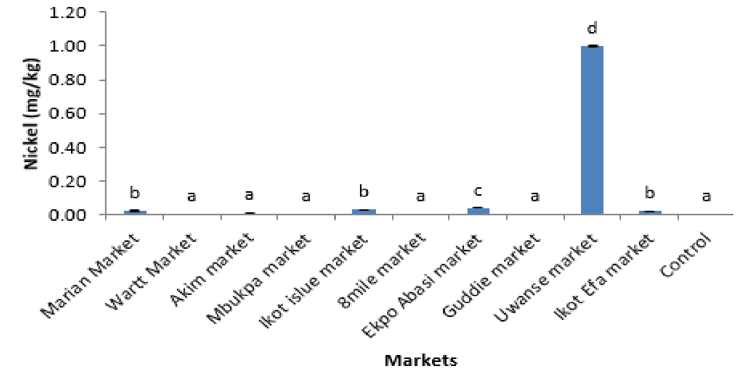

Fig 7 heavy metal composition (Nickel) of palm oil sold in Calabar metropolis

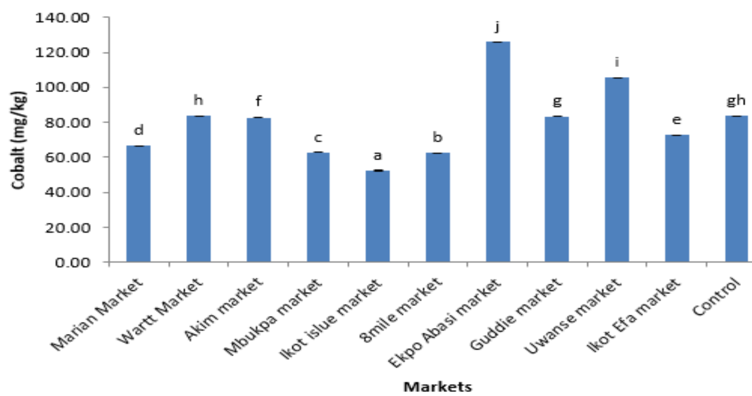

Fig 8 heavy metal composition (Cobalt) of palm oil sold in Calabar metropolis

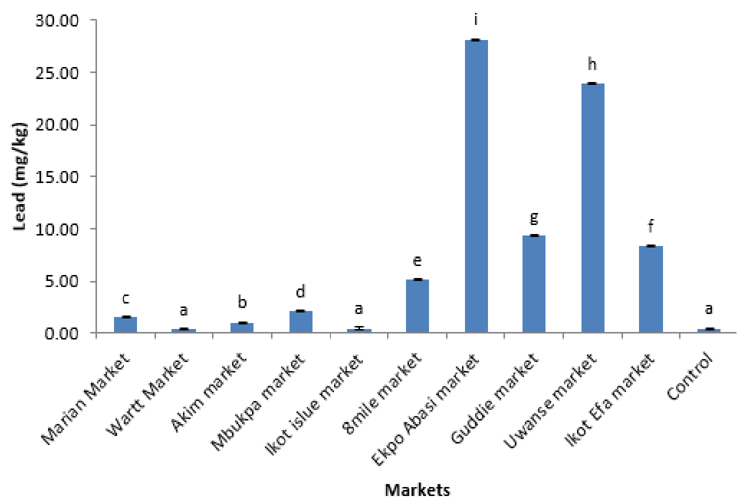

Fig 9 heavy metal composition (Lead) of palm oil sold in Calabar metropolis

Palm oil is highly nutritious hence all living things have a keen demand for it. The high demand for oil palm coupled with other uses of an oil palm tree and its economic values have resulted in the special attention given to the multiplication of the seed-bearing fruits. It is an important source of vitamin A, which has been indicated as a good agent of good eyesight, weight development, and disease resistance. Palm oil has the highest value of Free Fatty Acid (FFA) which shows that oleic acid is predominantly the free fatty acid present in palm oil. Oyenuga (1968), reported that low free fatty acid content indicated that the palm oil would not easily form rancidity when it was properly stored. From our results obtained from this work, the free fatty acid was above the acceptable limit and the maximum limit for free fatty acid at 5 % Ohimain and izah (2005). The free fatty acid obtained in the present research ranged between 4.12-9.26 MgKOH/g. These values may be higher due to the post-handling and display pattern in the market EkwenyeUN (2005). The acid value is an indication that could be used to measure Free Fatty Acid (FFA) content present in palm oil. However, when palm oil is exposed to a particular temperature it could result in increased acid value which is due to hydrolysis of glycerides. An increase in acid value could lead to increased susceptibility of the palm oil to rancidity. Again palm oil consumed by humans should not contain a high level of free fatty acids because the indication of free fatty acid in the palm oil may render unpleasant odor and deteriorate the quality of the palm oil. The increase in free fatty acid may be due to the different stages taken place in their methods of production as well as the point of sampling. In addition, the palm oil may be subjected to certain controlled conditions at the mills and the efficiency of the expelling machines being used. It is important to know that palm oil from factories is properly separated from moisture compared to locally produced palm oil Pearson (1976). Iodine value is an indication of unsaturation in the palm oil samples which is valuable for detecting adulteration in palm oil. The results obtained from this study show that the level of iodine value ranges between 21.40-45.78 MgKOH/g.

This result was compared to that of Orji and Mbata (2008). The increased value could show that deterioration has commenced in the sample collected. Ekwenye (2005). More so, the iodine value in palm oil shows some degree of unsaturation within the metropolis which could determine the level of susceptibility of the palm oil to rancidity. Therefore, excess amounts of iodine in the body can cause enlargement of the thyroid gland and the development of goiter. Peroxide value is used to know the level of palm oil oxidation which measures the freshness of the lipid and oxidation at a different level of storage depending on the activities of the lipolytic enzymes like lipoxgenase and peroxidase. From the result obtained the peroxide value ranged between 0.03-3.60 Meq/K which is comparable with the standard value of 10 MqKg SON/NIS (2005). In line with the result obtained from this research work, it could be deduced that the peroxide value was significantly higher in the palm oil samples in the selected market. The locally processed Nigeria palm oil falls within the range between (2.7-7.4 mg/KOH/g). Adding that peroxide value is correlated with the extent to which oxidative rancidity has occurred in the palm oil which is one of the important measures used to ascertain the shelf life of any palm oil. Heavy metals have been detected to be above the permissibility limit by WHO (2004). Heavy metals can bioaccumulation in the biological system and proffer a potential health risk to consumers over a long period. The concentration of heavy metals ranges from different levels based on the location of the palm oil sample in this research work. Zinc is a necessary heavy metal that is needed by the body. Prashanth (2005), reported that 15-20 mg of zinc is needed per day. From the results of these studies zinc concentration was significantly higher but within the standard limit. Zinc remains the most important nutrient for human health and is essential for the functioning of most metalloenzymes. An oral dose of zinc can cause symptoms including vascular shock, vomiting, dyspeptic nausea, diarrhea, tachycardia, pancreatic, and damage of hepatic parenchyma Salgueiro *et al.*, (2000). A high level of zinc could cause absorption via interaction with some metallothionein at the brush border of the intestinal lumen Sunderman (1981). Cadmium is another toxic heavy metal detected in this study from our results cadmium shows a significant increase across the selected markets compared with the control market, though within the reference range on the palm oil investigated. Cadmium exposure and its absorption in the lungs have been found to be between 10-50% while the absorption in the gastrointestinal tract is less. WHO 2004 reported that average intake or daily intake varies from about 10-40 ug in non-polluted areas and could affect the renal tubular damage in humans especially with a long daily intake of about 140-260 ug of cadmium. In addition, the concentration at which cadmium becomes toxic depends on the health and status of the person. Often at time cadmium could be nontoxic at a lower concentration in immune-compromised individuals than healthy individuals. Cadmium exposure from environmental contamination and other sources may develop at a much lower level. Results have shown that both humans and animals studies indicate that skeletal damage may be an effect of cadmium exposure from our ready-to-eat food WHO (2004). A practical example is through our food sources like the seed, root of plants, fruits, and even the leaves that we consumed on daily basis. Nickel is discharged into the environment annually from the combustion of fossil fuel. From our results on the present studies, nickel was significantly higher in one of the selected markets compared with the control. This implies that nickel was within the permissible limit; hence research has shown that the daily intake of Nickel in the human diet is about 165 mg Myron (1978). Repletion of nickel in plants suggests that nickel is a vital trace element in animals though its functional efficacy has not been indicated. Nickel is regarded as necessary because of its deficiency in animal spices, nickel shortage can be revealed formally in the liver but its effect includes abnormal cellular morphology, oxidative stress disruption in lipid level. Nickel could also cause a decrease in growth and hemoglobin condensation and devastated glucose metabolism ATSDR (2003). The concentration of cobalt in these studies was above the reference range. Cobalt is a component of cyanocobalim (Vit B12) and an essential element in the body. It is found in large concentration in the liver ATSDR (2004). Cobalt is involved in the synthesis of Vit B12 which is required for the production of red blood cells and the prevention of pernicious anemia in humans and animals. Cobalt was also found to be within the permissibility limit recommended by WHO. From other research work cited about 0.03 ug cobalt is present in micrograms in vitamin B12 and other organic compounds. It is also useful as a therapeutic agent for the treatment of anemia and cyanide poisoning. Increased levels of cobalt in food and water do not tend to accumulate within the human body. Cobalt is excreted out in urine, though another incidence reported on goiter was higher in some regions Wills (1966). Lead is the most ubiquitous toxic metal and can be detected partially in all components of the environment. Lead is a known neurotoxin that could bring about impairment in children and can also cause the mobilization from bones during pregnancy and lactation ATSDR (2004). Lead toxicity has long been associated with sterility and gemeto-toxic effect in both male and female animals. Some clinical studies have shown that lead is capable of passing through the placenta to fetus to cause developmental abnormalities during birth. Studies have also shown that an increased level of lead could cause chromosomal defects in workers and suppress the immune system as observed in experimental animals Deknudt (1977). From this study, the concentration of lead was above the permissibility limit.

Conclusion: This research work shows a detectable amount of some selected heavy metals in palm oil commonly sold in calabar metropolis. The results of the findings indicate that all the selected heavy metals were below the permissible limit Cobalt and lead were above permissibility limit. The high concentration of most of the selected parameters used on these studies may be due to some environmental factors, such as exposing the palm oil during processing, storage and packaging that could lead to the unsafe palm oil not suitable for consumption.

Acknowledgment: The author's wishing to thank the Department of Biochemistry for the freedom given to them to use their laboratory for this research work.

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