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Determination of Heavy Metals Levels in Palm Oil obtained from Ankpa, Olamaboro and Dekina Local Government Areas of Kogi State, Nigeria

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Abstract
This study aimed to determine the concentration of cadmium, chromium and lead in palm oil obtained from three local government areas in Kogi State, Nigeria (Ankpa, Olamaboro and Dekina). Forty-Eight (48) palm oil samples were purchased randomly from four (4) different market sellers from each council wards in Kogi State. The samples were digested and analyzed using Atomic Absorption Spectrometer (AAS). The order of abundance of the heavy metals analyzed in palm oil follows this order: Pb> Cr > Cd. The mean concentrations (mg/kg) of palm oil were recorded as: AnkpaPb(13.34±1.3), Cr(12.63±1.1), Cd(0.89±0.2), Dekina Pb(15.21±1.4), Cr(12.99±1.3), Cd(0.99±0.2) and OlamaboroPb(11.67±1.3), Cr(9.58±1.3), Cd(1.18±0.2) respectively which all exceeded the permissible limit set by WHO/FAO.Values of the physicochemical properties showed that the saponification value, iodine value, and peroxide value were all in good agreement with the FAO/WHO recommendation standards except free fatty acid and pH which were above the recommended value. The results obtained from this study suggest that the palm oil samples analyzed are detrimental to human health in terms of the metals of interest analyzed. Hence, awareness campaign must be created on the production of oil, storage and probably the rate of consumption.
Keywords: Palm oil, Heavy metals, AAS, Human Health Risk, Kogi State, Nigeria

Introduction

Palm is one of the most important crops in production and applications. Palm oil is produced from the mesocarp of the oil palm fruit (*Elaesisguineensis*). It also forms a vital crop in Southeast Asia, West Africa and South America especially due to its dietary and healing properties [1]. Palm also serves as an imperative remedy for different diseases in various parts of Africa [2]. Nigeria is among the most important producers andthe palm oil industry is a major agro based enterprise in Nigeria, especially in the southernpart where palm trees are found both in the wild and in plantations [3]. Palm oil is an edible vegetable oil that is naturally reddish in colour because of high beta-carotene content (a precursor of vitamin A), vitamin E, sterols, Phospholipids, glycolipids and squalene[4]. It also contains fatty acids and unsaponifiable constituents, other vital characteristics, which also have antioxidant activities, cholesterol lowering, anti-cancer and protection against artherosclerosis tendencies [5]. Palm oil and its products are useful for cooking/frying, in local dishes, in soap production, and as a source of vitamins A, E and K [6].

Heavy metals are another type of environmental contaminant. It has been reported that contamination of heavy metals in palm oil could result from different sources such as drinking water, high ambient air concentrations, industrial waste, acidic rain, soil breakdowns and food chain [7]. The contamination of a food chain with heavy metals could pose potential health risk to humans and animals because these heavy metals canbioaccumulate. They could also be leached from the processing equipment over time depending on the metalloid used in the production at the processing facilities [7].

Some heavy metals may access red palm oil during planting, harvesting, processing, packaging, storage or sale of the product [8]. However, their accumulation over time pose a potential health risk to humans who regularly consume red palm oil contaminated with toxic metals.

Therefore, it has become imperative to investigate the levels of heavy metals in palm oil sold in different markets in Kogi, Nigeria. Hence, this study aimed to assess the heavy metal levels (Cr, Pb and Cd) in palm oil from Kogi State using AAS.

Materials and Methods

Study Area

The study was conducted in Kogi State, Nigeria from three different local government areas Ankpa (located at 7^{0}22'14"N, 7^{0}37'31"E), Dekina (located at 7^{0}35'N, 7^{0}12'E) and Olamaboro (located at 7^{0}11'N, 7^{0}34'E) occupying a total area of 29,833 square kilometers with a population of 3,314,043 at the 2006 census. The three local government areas were chosen because of the abundance of oil palm plantations in the areas and the palm oil processing is mostly by traditional methods. The map of Kogi State showing the sampling areas are shown in Figure 1.

Sample Collection

Fresh palm oil samples were obtained from three local government areas (Ankpa, Dekina and Olamaboro) in Kogi State, Nigeria. The palm oil samples were randomly purchased from four different market sellers from each council wards in Kogi State. The collected palm oil samples were packed in polyethylene bottles and stored below 20°C until analysis for heavy metal determinations. All plastics and glassware were cleaned and soaked in nitric acidsolution overnight and rinsed with distilled water.

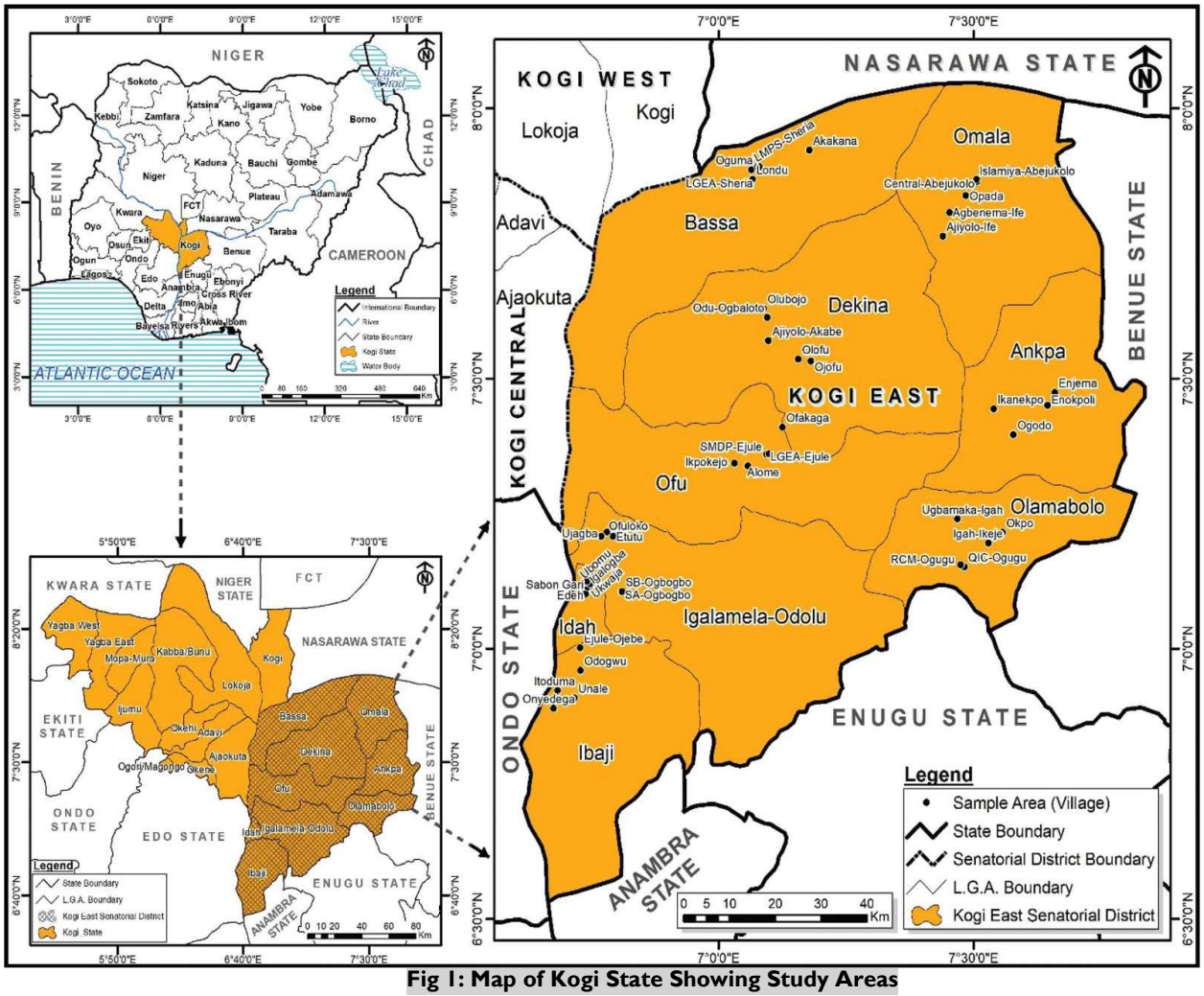

Fig 1: Map of Kogi State Showing Study Areas

Sample Digestion

Exactly 1.0 g each of the samples were weighed and transferred quantitatively into a 250 mL conical flask and 10 mL of the digestion acid mixture in the ratio (1:2:2) of perchloric, nitric and sulphuric acids was added to the sample and heated on a hot plate in a fume hood. The mixture was heated until a white fume was observed which signified that digestion was complete. The sample was allowed to cool and 20 mL of distilled water was added to bring the metals into solution. Sample was allowed to cool to room temperature and filtered through a Whatman No. 42 filter paper into 100 mL volumetric flask and made up to mark with distilled water. A reagent blank containing acid mixtures used was prepared. The

elements determined were: Cr, Pb and Cd using Atomic Absorption Spectrophotometer Phoenix 986 (Biotech Engineering Management Co. Ltd. UK) following standard procedures.

Method Validation and Quality control for Metal Analysis

In order to validate the analytical method, the following method validation parameters such as instrumental detection limit, limit of detection, limit of quantification, precision and accuracy studies were carried out [9]. All

reagents and chemicals used were all analytical grade; glass wares used during the laboratory analysis were thoroughly washed with several changes of HNO_3 and properly rinsed several times using deionized water. A blank solution and standards were analysed in order to ensure precision and accurancy of the determinations.
Limit of detection (LOD) is the minimum concentration of analyte that can be detected but not necessarily quantified with an acceptable uncertainty. LOD for each metal was determined from the analysis of seven replicates of method blanks which were digested in the same digestion procedure as the actual samples. This was represented as;

$$LOD = 3 \times S_{bl} \quad (1)$$

Where:
S_{bl}= is the standard deviation of the method blank solution[10].
The limit of quantification (LOQ) is the lowest concentration of an analyte in a sample which can be quantitatively determined with acceptable uncertainty. LOQ was obtained from triplicate analysis of seven method blanks digested in the same digestion procedure as the actual samples. This is representedas;

$$LOQ = 10 \times S_{bl} \quad (2)$$

Where:
S_{bl} =is the standard deviation ofthe method blank solution [11].

Statistical Analysis
Statistical analysis involved the determination of mean, standard deviation, minimum, maximum, significant differences and ANOVA. In order to meet the principles of the analysis of variance (additivity, homogeneity of variance and normality of distribution), the data were subjected to logarithmic transformations prior to the results.

Results and Discussion
The physicochemical properties of palm oil must be carried out to determine the qualitative and quantitative properties of produced palm oils. Table (1) shows the physicochemical properties of palm oil.

Table 1: Mean Physiochemical Parameters of palm oil

Locations	pH	PV mmol/kg	IV g/100g	SV mgKOH/100g	FFA mgKOH/100g	Viscosity mm^2/s
Ankpa	6.04±1.94	5.07±0.02	49.09±0.72	194.29±5.02	37.38±0.32	36.07±0.18
Dekina	6.43±1.47	5.72±0.04	50.46±1.30	202.86±2.55	46.19±0.1	36.17±0.13
Olamaboro	6.36±1.22	6.22±0.01	55.04±1.01	199.31±3.68	47.12±1.1	36.83±0.11

PV: Peroxide Value, **IV**: Iodine Value, **SV**: Saponification Value and **FFA**: Free Fatty Acid
The result obtained (Table 1), showed that Saponification value (SV) ranged from 194.29-202.86 mgKOH/g of oil, iodine value are in the range of 49.09-55.04 g/100g, 36.07-36.83 mm^2/s values were obtained for viscosity, peroxide value was obtained as 5.07-6.22 mmol/kg, free fatty acid were found as 37.38-47.12 mgKOH/100g and pH ranged from 6.04-6.43 .

Mean Concentrations of Heavy Metals Palm Oil
Summary statistics of Pb, Cr and Cd concentrations in the study areas were expressed in mean values with their respective standard error (Table 2). There was no significant difference in heavy metal concentrations in palm oil collected from the 3 study locations, $P < 0.05$.

Table 2: Mean Concentrations of Heavy Metals (mg/kg) in Palm oil in the Study Areas

Study Areas/Heavy Metals	N	Mean ± Std. Error	Minimum	Maximum
Ankpa				
Pb	16	13.34± 1.3	3.35	23.35
Cr	16	12.63 ± 1.1	3.40	20.45
Cd	16	0.89 ± 0.2	BDL	3.00
Dekina				
Pb	16	15.21 ± 1.4	3.35	23.35
Cr	16	12.99 ± 1.3	3.40	20.45
Cd	16	0.99 ± 0.2	BDL	3.0
Olamaboro				
Pb	16	11.67 ± 1.3	BDL	20.00
Cr	16	9.58 ± 1.3	BDL	20.45
Cd	16	1.18 ± 0.2	BDL	2.57

BDL: Below detection limit

Lead

The Pb (Lead) concentration ranged from 11.67 to 15.21 mg/kg. From my research findings,Pb has the highest concentration from all collected palm oil samples in Dekina with a mean concentration of 15.21 ± 1.4 (mg/kg), while the lowest concentration of 11.67 ± 1.3mg/kg was found in the samples from olamaboro. The concentration of Lead obtained in this study is above the permissible or acceptable limit by [12].The study by [13] reported a Lead level of 0.028 – 0.064 mg/kg in Iran which is lower than the current research work. [2]and[14] also reported a low Pb concentration of (0.0225-0.038mg/kg and 0.024-0.067 mg/kg) respectively, in palm oil bought from several markets in Lagos, Nigeria and in palm oil from South-Eastern.On the other hand, Lead concentration (25.00 – 30.00) mg/kg obtained by [15] recorded higher value than the current research work.

Lead has harmful health effects even at lower levels and there is no known safe exposure level [16].This means that even the low concentration of lead in some of the research work reviewed in palm oil is detrimental to health if the oil samples are consumed for a very long time since lead can show an accumulated harmful effect. This result may result inpossible neurological damage to foetuses, abortion and other complications in children [17].

Chromium

In this study chromium concentration has the second highest value mean concentration in the three local government areas as shown in Table (2). The mean concentration of chromium ranges from 9.58 – 12.99 mg/kg. The chromiumconcentration recorded in this study exceeded the permissible or acceptable limit by WHO/FAO. The mean value obtained in this study area is higher than the values reported by [18] 0.021 – 0.033 mg/kg and also results reported by [14] who worked on palmoil samples from South-Eastern Nigeria (0.101-0.298 mg/kg).

Chromium (VI) is considered carcinogenic to humans. Chromium (VI) toxicity is due to its strong oxidation property. It affects the kidneys, theliver and blood cells through oxidation reactions leading to haemolysis,renal and liver failure. Nevertheless, aggressive dialysis can improve this situation, while $Chromium^{+3}$ is less detrimental to health due to its absorption by the body (<1%) [19].

Cadmium

Cadmium in this studycadmium has the lowest mean concentration among all the three metals. The mean concentration value of cadmium obtained in this study area is above the maximum permissible limit in palm oil, suggesting that it may be detrimental to health when consumed in higher quantities.[2] reported a Cd concentration of 0.025-0.065 mg/kg and [20] recorded 0.064 ± 0.020 mg/kg in the Evaluation and Risk Assessment of Selected Heavy Metals and Essential Elements in Crude Palm Oils from Oil Mills in South- West and South-South Nigeria which are all lower than the results of this study.

Cadmium is known to exert adverse effects on brain metabolism and other severeeffects such as prostate cancer, and could also cause kidney, liver, lungs, and bone damage[21].

Metals play an important negative and positive role in human life. From the results obtained in this study, the levels were above tolerable limits for human intake and could pose toxicological health concern [22].

Quality Control Parameters in Palm Oil

Table (3) shows the limit of detection (LOD), limit of quantification (LOQ) and the relative standard deviation (R.S.D) obtained from heavy metals.

Table 3: Mean Concentrations and Relative Standard Deviation of Metals determined in palm oil

	Quality Control Parameters				
Metals	**Mean (ppm)**	**S.D**	**LOD (ppm)**	**LOQ (ppm)**	**R.S.D (%)**
Lead	3.3417	0.04600	0.1380	0.460	1.37
Chromium	3.4050	0.00187	0.0561	0.187	0.05
Cadmium	0.4117	0.02320	0.0696	0.232	5.63

The quality control parameters of metals (Pb, Cr and Cd) are presented in Table 3. The RSD ranged from 0.054 % to 1.37 %, LOQ ranged from 0.187 to 0.460 ppm and LOD ranged from 0.0561 to 0.138 ppm. The LOQ and LOD method were low enough to detect and quantify the presence of metals of interest in the samples. Based on LOD and LOQ values, AAS was sensitive enough toanalyze these heavy metals because the values were lower than the maximum values of metals in the samples.

Conclusion

The palm oil samples collected from three local government areas were analyzed using Gas Atomic Absorption Spectrometry (AAS).

The results in this study also reveal that the analysis of heavy metals was present in palm oil samples. The heavy metals concentration of cadmium, chromium and Lead all exceeded the permissible or acceptable limit set by WHO/FAO which can be very dangerous to human health. Values of the physicochemicalproperties showed that the saponification value, iodine value, and peroxide value were all in good agreement with the FAO/WHO recommendation standards. While free fatty acid and pH are above the recommended value according to FAO/WHO and this can be attributed to over ripening of the palm fruits which the palm oil was extracted.

The monitory of toxic metals in oil is essential or important in order to prevent excessive build-up of these pollutants in human food chain.

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Competing Interests

Authors have declared that no competing interests exist.

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