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Evaluation of the Concentration of Some Toxic Metals in Dietary Red Palm Oil

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Abstract

Palm oil has been part of human diet for more than 5000 years. For generations, it has been revered as both a nutritious food and a valuable medicine. However, care should be taken to evaluate the purity and safety of this nutritional and medicinal agent to the human system. This study investigated the concentration of cadmium, chromium, mercury, lead, arsenic and nickel in twenty-five samples of ready-to consume palm oil that were bought randomly from different markets in Lagos, Nigeria. The samples were digested with aqua-regia (2:1:2 HNO $_3$:HClO $_4$:H $_2$ SO $_4$ respectively) and the digested samples were analyzed using Atomic Absorption Spectroscopy. There was no detectable mercury in one of the twenty-five samples analysed. However, all the samples contained a detectable amount of each of the other five metals analysed. The Oral Component Limit (OCL) for cadmium, chromium, mercury, lead, arsenic and nickel as stated by USP are 0.5µg/g, 25 µg/g, 1.5 µg/g, 1.5 µg/g and 25 µg/g respectively. The samples contained detectable amounts of the metals although with values below the USP standard OCL. The results obtained from this study suggest that the palm oil samples analysed are save for consumption in terms of the metals of interest analysed.

Keywords: Palmoil; Heavy metals; Bioaccumulation; Contamination; Medicinal agent; Health risk.

Introduction

Palm oil is produced from the oil palm fruit *Elaesis guineensis*). It forms a vital crop in Southeast Asia, West Africa and South America especially due to its nutritional and healing properties [1,2]. History has it that palm oil serve as important medicinal remedy for different diseases in various parts of Africa. Palm oil is viewed locally as essential in the diet of pregnant and nursing women in order to ensure good health for the mother and child [3,4]. Interestingly, both government and health professionals have recognized health benefits of palm oil in the treatment and prevention of malnutrition and vitamin A deficiency diseases [1,2]. Red palm oil is rich in antioxidant vitamins, trace elements and supplies fatty acids essential for proper growth, development and for general well-being.

It has been reported that contamination of diets including red palm oil with heavy metals could result from different sources such as drinking water, high ambient air concentrations, industrial waste, acidic rain breaking down soils and food chain [5,6]. Contamination of the food chain with heavy metals could pose potential health risk to humans and animals because these heavy metals have the ability to "bioaccumulate". Bioaccumulation means an increase in the concentration of a chemical in a biological organism over time, compared to the chemical's concentration in the environment. Reports from previous research have shown that compounds accumulate in living things any time they are taken up and stored faster than they are broken (metabolized) or excreted) [5].

Although red palm oil remain vital in human nutrition and medicinal treatment, we are concerned about its contamination by toxic elements and the potential risk such contamination could pose to the consumers in our locality. To the best of our knowledge no study has been conducted in our environment to evaluate the concentration of heavy metals present in red palm oil and the potential hazards such contamination may pose to human health. It is possible that these heavy metals could have access into red palm oil during planting, harvesting,

processing, packaging, storage or sale of the product. The presence of these toxic metals may appear harmless in minute quantities, however their accumulation over time carries potential health risk to human who regularly consume red palm oil contaminated with toxic metals. Therefore, it has become imperative to investigative the levels of heavy metals in red palm sold in different markets in Lagos, Nigeria. Lagos is the commercial city of Nigeria and red palm oil from different parts of the country are readily sold in Lagos, making Lagos an important location to conduct this study. The study examined the occurrence and the concentrations of toxic metals: arsenic, cadmium, lead, mercury, nickel and chromium in twenty five samples of locally produced palm oil.

Materials and Methods

Sample collection

The abundance of palm oil in Nigeria was exploited. Various markets were visited and twenty-five (25) samples from about ten (10) palm oil producing states were bought and analysed. The states include Ogun, Ondo, Ekiti, Oyo, Edo, Cross River, Delta, Imo, Enugu and Elbonyi.

Preparation of standard solutions for heavy metals

Fishers Scientific Reference AAS standard solution (Ohio, USA) of

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chromium, mercury, lead, nickel, arsenic and cadmium, 1000 ppm, was diluted to the desired concentrations by serial dilution. The standard solution of each metal, 25 ml, was pipetted into a 250 ml volumetric flask and made up to volume with ultra-pure water (100 ppm stock standard) and the following working standard 0.5, 1.0, 1.5, 2.0, 4.0, 6.0, 8.0 ppm were prepared via serial dilution. Table 1 presents the regression equations, Pearson's correlation coefficient and coefficient of determination obtained from the calibration plots.

Digestion of samples for metal analysis

All the samples were digested using the same method. Each sample, 5.0 g, was carefully weighed into a digestion tube. A solution of nitric acid, perchloric acid and sulphuric acid was prepared in the ratio 2:1:2 (0.5N nitric acid, 1N perchloric acid and 1M sulphuric acid all from British Drug House (BDH), United Kingdom). The acid mixture, 10 ml, was carefully measured in a fume cupboard and added to the sample in the digestion tube (Pyrex^(R)). This was digested at a temperature of 250°C for two and half hours to obtain a completely digested clear solution. It was cooled to room temperature, made to 50 ml with ultra pure water, transferred to a set of centrifuge tubes and shaken on a mechanical shaker for ten minutes. It was then centrifuged for five minutes at 5000 rev/min and the digest was sampled to a set of vials and stored for elemental analysis. The acid mixture, 10 ml, was also digested following the same procedure and was used as blank. The samples were determined using atomic absorption spectroscopy (AAS). All the acids used are from the British Drug House (BDH), United Kingdom.

Analysis of heavy metals

The analysis of chromium, lead, mercury, arsenic and nickel was carried out with a Buck Model 205 atomic absorption spectrophotometer, USA. In all cases, air-acetylene was the flame used and hollow cathode lamp of the individual metals was the resonance line source. The calibration plot method was adopted for the analysis [7,8]. For each element, the instrument was auto zeroed using the blank (de-ionized water) after which the standard was aspirated into the flame starting from the lowest concentration. The corresponding absorbance values were obtained and the graph of absorbance against concentration was plotted by the instrument. The digested samples were then analyzed in duplicates with the average concentration of the metal present being displayed in part per million (ppm) by the instrument after extrapolation from the standard curve. For arsenic measurement, hydride generator was attached to AAS while cold vapour technique attached to AAS was used to estimate mercury [9].

Results

The regression equations, Pearson's correlation coefficient and coefficient of determination obtained from the calibration plots for chromium, mercury, lead, nickel, arsenic and cadmium are shown in table 1. The results obtained for the concentration of the metals in the palm oil samples are shown in table 2. After calibrating the system

with the standard solutions, the spectrophotometer automatically determined the concentration of each metal present in the digested solution of the palm oil samples by extrapolation in part per million (ppm). For the purpose of referencing to standard limits, the results are presented in µg/g concentrations of their corresponding samples. The concentration of chromium in the samples ranged from 0.021 to 0.033 µg/g, mercury ranged from 0.01 to 0.055 µg/g, lead from 0.0225 to 0.038 µg/g, nickel from 0.0435 to 0.068 µg/g, arsenic from 0.001 to 0.0025 µg/g and cadmium from 0.025 to 0.065 µg/g.

Discussion

The current study shows that red palm oil sold at different Lagos markets has detectable levels of selected heavy metals below the USP standard OCL. However, since these metals can bio-accumulate in the biological system over time, it carries a potential health risk to regular consumers of the oil over long period of time. The concentration level of chromium in each sample ranged from 0.021 to 0.033 $\mu g/g$, mercury ranged from 0.01 to 0.055, lead from 0.0225 to 0.038, nickel from 0.0435 to 0.068, arsenic from 0.001 to 0.0025 and cadmium from 0.025 to 0.065. Chromium, lead, nickel, arsenic and cadmium were detected in all the 25 samples and mercury was detected in 24 samples. However, with reference to the information in table 3, all the metals have concentrations below the USP OCL. All the samples contained detectable amounts of one or more of the metals of interest with 24 samples containing all the 6 metals.

Cadmium is one of the toxic metals detected in the red palm oil that was investigated and it has been shown that diet is the main source of cadmium exposure and that the absorption of cadmium in the lungs has been found to be 10-50% while the absorption in the gastrointestinal tract is less. According to the WHO report (1992), average daily intakes vary considerably from about 10 to 40 μg in non-polluted areas to several hundreds of micrograms in cadmiumpolluted regions. WHO (1992) further stated that signs of renal tubular damage occur in humans with a life-long daily intake of about 140-260 µg of cadmium or a cumulative intake of about 2000 mg. It should also be noted that the concentration at which cadmium becomes toxic is dependent on the health status of individuals. For instance, cadmium could be more toxic at a lower concentration in immunecompromised persons than in healthy immune-competent persons. According to available report, renal tubular damage is probably the critical effect of cadmium exposure in the general population and those exposed to environmental contamination and that tubular damage may develop at much lower levels than previously estimated [10]. Data from several reports from different countries indicate that an average urinary cadmium excretion of $2.5 \mu g/g$ creatinine is related to an excess prevalence of renal tubular damage of 4% resulting from long term intake. Both human and animal studies indicate that skeletal damage may be a critical effect of cadmium exposure and that cadmium may be classified as probable human carcinogen group 2A highlighting the danger of bioaccumulation of cadmium over a long period of time

Metal	Chromium	Mercury	Lead	Nickel	Arsenic	Cadmium
Regression equation	y=0.1x + 4E-05	y=0.101x-0.0016	y=0.1x+0.0001	y=0.1x- 0.0002	y=0.2001x+6E-05	y=0.2x+0.0001
Coefficient of determination (R²)	1	0.9999	1	1	1	1
Pearson's correlation coefficient	0.9999	0.9999	0.9999	0.9999	0.9999	0.9999

 Table 1:
 Regression Data for the Analysis of the Metal ion Standard Solutions.

Sample	Average Conc. of Cr (μg/g) ± SD	Average Conc. of Hg (μg/g) ± SD	Average Conc. Pb (μg/g) ± SD	Average Conc. Ni (μg/g) ± SD	Average Conc. As (μg/g) ± SD	Average Conc. Cd (µg/g) ± SD
P1	0.021 ± 0.0028	0.01 ± 0	0.0275 ± 0.0091	0.0435 ± 0.0106	0.0015 ± 0.0007	0.055 ± 0.0070
P2	0.022 ± 0.0056	0.015 ± 0.0070	0.035 ± 0.0070	0.0455 ± 0.0049	0.0015 ± 0.0007	0.045 ± 0.0070
Р3	0.0255 ± 0.0063	0.015 ± 0.0070	0.0275 ± 0.0021	0.053 ± 0.0183	0.0015 ± 0.0007	0.045 ± 0.0070
P4	0.026 ± 0.0098	0.02 ± 0.0141	0.038 ± 0.0056	0.054 ± 0.0141	0.002 ± 0.0014	0.05 ± 0
P5	0.022 ± 0.0000	0.01 ± 0.0141	0.0345 ± 0.0120	0.046 ± 0.0056	0.002 ± 0	0.065 ± 0.0212
P6	0.0255 ± 0.0007	0.015 ± 0.0212	0.0305 ± 0.0035	0.0525 ± 0.0063	0.0015 ± 0.0007	0.065 ± 0.0212
P7	0.024 ± 0.0070	0.025 ± 0.0070	0.038 ± 0.0014	0.0495 ± 0.0077	0.0015 ± 0.0007	0.045 ± 0.0070
P8	0.0255 ± 0.0049	0.025 ± 0.0070	0.0225 ± 0.0035	0.053 ± 0.0155	0.001 ± 0	0.04 ± 0
P9	0.033 ± 0.0014	0.035 ± 0.0212	0.033 ± 0	0.068 ± 0.0084	0.001 ± 0.0014	0.035 ± 0.0070
P10	0.029 ± 0.0113	0.04 ± 0.0141	0.034 ± 0.0113	0.0595 ± 0.0176	0.0015 ± 0.0007	0.04 ± 0.0141
P11	0.026 ± 0.0028	0.02 ± 0.0141	0.0325 ± 0.0077	0.0535 ± 0.0120	0.002 ± 0.0014	0.05 ± 0
P12	0.024 ± 0.0098	0 ± 0	0.0315 ± 0.0063	0.0495 ± 0.0148	0.002 ± 0	0.04 ± 0.0141
P13	0.0215 ± 0.0021	0.03 ± 0.0424	0.026 ± 0.0098	0.044 ± 0.0098	0.002 ± 0.0014	0.035 ± 0.0070
P14	0.024 ± 0.0028	0.05 ± 0	0.0295 ± 0.0035	0.049 ± 0	0.002 ± 0	0.035 ± 0.0070
P15	0.024 ± 0.0014	0.025 ± 0.0353	0.03 ± 0.0070	0.0495 ± 0.0035	0.0015 ± 0.0007	0.03 ± 0
P16	0.022 ± 0.0056	0.02 ± 0.0282	0.0315 ± 0.0077	0.046 ± 0.0056	0.002 ± 0.0014	0.035 ± 0.0070
P17	0.0245 ± 0.0049	0.03 ± 0.0141	0.0285 ± 0.0035	0.051 ± 0.0155	0.002 ± 0	0.045 ± 0.0070
P18	0.0255 ± 0.0077	0.035 ± 0.0212	0.03 ± 0.0028	0.051 ± 0.0127	0.0015 ± 0.0007	0.05 ± 0
P19	0.0255 ± 0.0063	0.055 ± 0.0070	0.0285 ± 0.0035	0.0515 ± 0.0162	0.002 ± 0.0014	0.05 ± 0
P20	0.031 ± 0.0014	0.05 ± 0	0.0315 ± 0.0035	0.0615 ± 0.0007	0.002 ± 0	0.045 ± 0.0070
P21	0.029 ± 0.0014	0.05 ± 0	0.028 ± 0.0014	0.0575 ± 0.0091	0.0015 ± 0.0007	0.04 ± 0
P22	0.0315 ± 0.0021	0.045 ± 0.0070	0.03 ± 0.0014	0.047 ± 0.0070	0.0025 ± 0.0007	0.04 ± 0.0141
P23	0.029 ± 0.0014	0.04 ± 0	0.029 ± 0.0028	0.057 ± 0.0042	0.002 ± 0.0014	0.04 ± 0
P24	0.0285 ± 0.0021	0.05 ± 0.0141	0.026 ± 0.0014	0.051 ± 0.0014	0.0025 ± 0	0.04 ± 0
P25	0.0315 ± 0.0021	0.055 ± 0.0070	0.032 ± 0.0014	0.057 ± 0.0042	0.002 ± 0.0007	0.025 ± 0.0353

Table 2: Determined Heavy Metal Concentration for Each Sample in $\mu g/g \pm SD$.

Metals/ Parameters	Oral RFD (μg/kg/day)	Recommended Daily Oral Dose* PDE (μg/day)	Oral Component Limit (OCL) (μg/g)	Parenteral Component Limit (PCL) (μg/g)	
Chromium	5	250	25	2.5	
Mercury	0.3	15	1.5	0.15	
Lead	0.2	10	1	0.1	
Nickel	5	250	25	2.5	
Arsenic	0.3	15	1.5	0.15	
Cadmium	0.1	5	0.5	0.05	

^{*}Recommended daily oral dose based on a 50 kg person

Table 3: Elemental Impurities Guidelines (DeStefano et al, 2010).

[10]. For safety of human health, various regulatory organizations such as USP, BP, EPA, WHO, USEPA have set up parameters to limit the presence of heavy metals in palm oil. Parameters such as permissible daily exposure (PDE), rationale for reference doses (RFD's), oral component limit (OCL) and parenteral component limits (PCL)

are guidelines set to regulate elemental contaminations in different products including palm oil.

Lead, a ubiguitous and versatile metal was also detected in the red palm oil examined. It has become widely distributed and mobilized in the environment and human exposure to and uptake of this nonessential element has consequently increased [5]. At high levels of human exposure, there is damage to almost all organs and systems, most importantly the central nervous system, kidneys and blood, culminating in death at excessive levels. At low levels, haem synthesis and other biochemical processes have been reported to be affected by lead contamination [12-14]. Lead continues to be a significant public health problem in developing countries where there are considerable variations in the sources and pathways of exposure, therefore care need to be taking in the processing and handling of red palm in order to reduce contamination from the environment.

The central nervous system and the kidneys are well known critical organs with respect to exposure to mercury and is also known to affect the immune system [11] indicating the adverse effects of mercury in human health. The toxicity and carcinogenicity of nickel and nickel compounds including the oxidative mechanism in experimental animals and humans have also been established. Nickel has been shown to inhibit mitochondrial succinate dehydrogenase activity in rat lung epithelial cells and has been shown to alter intracellular calcium homeostasis and induce lipid peroxidation in humans [7,15,16]. Long-term ingestion of inorganic arsenic causes multi-system adverse health effects such as vascular disease, renal disease, chronic lung disease and liver disease [6].

Exposure to arsenic may lead to progressive peripheral and central nervous changes, such as sensory changes, numbness and tingling, and muscle tenderness. A symptom typically described is a burning sensation ("needles and pins") in hands and feet. Neuropathy is usually gradual and occurs over several years. Excessive darkening of the skin (hyperpigmentation) in areas that are not exposed to sunlight, excessive formation of skin on the palms and soles (hyperkeratosis), or white bands of arsenic deposits across the bed of the fingernails (usually 4-6 weeks after exposure) may occur [17].

The symptoms of exposure to some poisonous nickel compounds include nausea, vomiting, headaches and sleeplessness. The symptoms get worse later on from 12 to 24 hours after exposure and include a speeding heart, difficult breathing, chest pains and extreme fatigue. Nickel is rarely poisonous, but certain nickel compounds are extremely dangerous. The most common is nickel carbonyl in refineries, nickel mines and plating factories [9].

Chromium (VI) is carcinogenic [18]. The toxicity of chromium (VI) is due to its strong oxidation property. It damages the kidneys, the liver and blood cells through oxidation reactions leading to haemolysis, renal and liver failure. However, aggressive dialysis can improve this situation.

Factors influencing the toxicity of metals include: Interactions with essential metals, formation of metal-protein complexes, age and stage of development, lifestyle factors, chemical form or speciation and Immune status of host [19].

It is known that significant percentage of Nigerian population consume red palm oil both as nutritional and medicinal agents. It is good news that the palm oil samples analysed contained these toxic metals of interest at concentrations lower than the USP specification but if accumulated in the body over time may pose a risk to the health of consumers after many years.

Conclusion and Recommendation

This research showed detectable amounts of arsenic, cadmium,

lead, mercury, nickel and chromium in the palm oil samples, but none exceeded the USP Oral Component Limit (OCL). This shows that the regulatory bodies in Nigeria are doing a great work in ensuring that the palm oil obtained from the market are safe for human consumption. However, slow excretion of these metals may pose health risk through accumulation in the body over time.

The essence of producing and consuming palm oil is to achieve a desired nutritional and medicinal effect. We conclude that the locally produced palm oil samples analysed are safe in terms of the concentration of the metal ions of interest in this study.

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