

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

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Abstract

Crude palm oil (product of *Elaeis guineensis* Jacq Arecaceae) is a staple food in Nigeria and the whole world, being consumed for its nutritive values. This study aims to evaluate the levels of some heavy metals and essential elements in crude palm oil from fifty (50) sampling sites located along the roads in South-West and South-South Nigeria, cutting across five States (Oyo, Osun, Ondo, Bayelsa and Rivers States). The samples were digested using mixture of acids (HNO_3 : HClO_4 : H_2SO_4 in ratio 1:1:1) and analyzed using Flame Atomic Absorption Spectrometer (GBC Avanta PM A6600). The mean concentrations obtained in mg/L were in the ranges: Ca (23.19-47.41), Mg (5.15-8.28), Na (6.39-13.72), K (15.65-34.96), Fe (34.49-56.14), Mn (0.47-1.98), Ni (0.33-0.65), Cr (0.16-0.31), Pb (<0.001-0.02), Cd (<0.001-0.03), Cu (0.33-1.28), As (<0.001), Zn (3.53-10.09) and Al (1.18-3.12). The estimated dietary intake (EDI) in ($\mu\text{g}/\text{kg}$ bw/day) ranges were: Ca (2.443-4.996) Mg (0.543-0.770), Na (0.674-1.446), K (1.648-3.664), Fe (3.635-5.916), Mn (4.10E^{-2} -0.209), Ni (3.30E^{-2} - 6.80E^{-2}), Cr (1.60E^{-2} - 6.70E^{-2}), Pb (1.10E^{-4} - 3.99E^{-4}), Cd (1.10E^{-4} - 8.88E^{-4}), Cu (3.41E^{-2} -0.134), As (9.02E^{-5} - 1.10E^{-4}), Zn (3.63E^{-1} -1.062) and Al (3.00E^{-4} -0.329). The estimated target hazard quotient (THQ) and the total health risk index (HRI) values indicated no lifelong health concern of metals associated with the consumption of these locally produced crude palm oil samples since the THQ and HRI are less than one (<1). The results revealed differences between the South-Western States (Oyo, Osun and Ondo) and the South-South States (Rivers and Bayelsa) in the levels of Ca, K and Pb, while there was no significant difference in Fe, Cr, Cu, Cd, As for all the States. This can be ascribed to the different methods of palm oil production in the various States. The levels of the parameters determined show that the crude palm oil would contribute to dietary intakes of macro (Ca, Mg, Na, K) and micro (Fe, Mn, Ni, Cr, Cu, Zn) essential elements, while the levels of heavy metals (Pb, Cd, Al and As) were low in comparison with WHO limits, and therefore safe for consumption.

Keywords: Crude Palm Oil, Essential Elements, Estimated Daily Intake, Target Hazard Quotient, Health Risk Index,

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I. Introduction

Palm oil is produced from the oil palm fruit (*Elaeis guineensis* Jacq Arecaceae). It requires climatic conditions of between 1800 to 5000 mm of rainfall per year, temperature range of 17-28 °C and relative humidity above 75% to flourish (Poku, 2002). The oil palm is propagated by seedling and requires nursery period of 9-12 months before it is planted. Its fruiting begins from between 3-5 years and reaches optimal yield at 10 years after cultivation. It is an economic tree that has a life span of about 200 years, but its economic life is usually between 20 to 30 years (Matthew, 2009). It forms a vital crop in Southeast Asia, West Africa and South America especially due to its nutritional and healing properties (Edem, 2002).

Major players in palm oil production in the world are Indonesia, Malaysia, Colombia, Thailand and Nigeria. Meanwhile, Nigerian oil palm belt covers twenty-four States of South-western, South-South, South-Eastern States, where palm trees are found both in the wild and in plantations and about 80% of the oil palm industry dominated by small holders who are in major agro-based enterprise, using rudimentary and semi-mechanized equipment for processing (Nwaugo *et al.*, 2008, Ohimain and Izah., 2013).

Palm oil processing is carried out using large quantities of water in mills where crude or virgin oil is extracted from the palm fruits and is widely used in African cooking. The refined edible palm oil is utilized in food, pharmaceutical, cosmetics and other industrial processing activities (Adepoju Bello *et al.*, 2012) which brought the domestic consumption of palm oil in Nigeria in 2016/2017 and 2017/2018 to about 1.34 and 1.40 million metric tons respectively (Statista, 2018).

Crude palm oil or Vegetable oils may be contaminated by heavy metals through migration from arable soil (use of fertilizer, location of plantation and processing palm oil mills along highways), technological/ production processes, packaging and storage (Adepoju-Bello *et al.*, 2012; Szyzewski, 2016; Izah and Ohimain, 2016). These metals can equally enter the human body via food. Living organisms however, require varying amounts of these metals. Iron, cobalt, copper, manganese, molybdenum, manganese, chromium, and zinc, but in small amounts to perform some biological activities. Humans are also responsible for altering the chemical forms of heavy metals released to the environment and such alterations often affect a heavy metal's toxicity by allowing it to bio-accumulate in plants and animals, bio-concentrate in the food chain, or attack specific organs of the body. Some heavy metals such as mercury and lead are toxic metals that have no known vital or beneficial effect on organisms, and their accumulation over time in the bodies of animals can cause serious illnesses (Strömrgren, 1998) hence the necessity to evaluate the concentration of the heavy metals and other essential elements, estimate dietary intake and risk assessment of some selected elements in crude palm oil obtained from local mills located along the traffic route in the southern Nigeria.

II. Materials And Methods

2.1 Sampling and Sampling Locations

Crude palm oil samples were collected in amber glass bottles neatly washed and oven dried from local palm oil mills located along the roads from Ogbomosho-Ilajue (Oyo State), Ifon-Orolu-Osogbo- Sekona-Ile-Ife-Ondo road (Osun State), Oke Ogbomosho-Ondo-Ore junction-Akinjagunla on East-West road (Ondo State), Amassoma-Yenagoa- Azikoro- Otuokpoti- Onuebum-Otuoke-Emeyal- Elebele road (Bayelsa State) and Okubie-Ahoadia-Elele-Alimini on East-West road (Rivers State) South-West and South-South, Nigeria. The samples were collected from November 2018 to January 2019. Ten (10) samples were collected from each State making a total of 50 samples in all. The sampling sites in the various States are as illustrated in Figure 1.

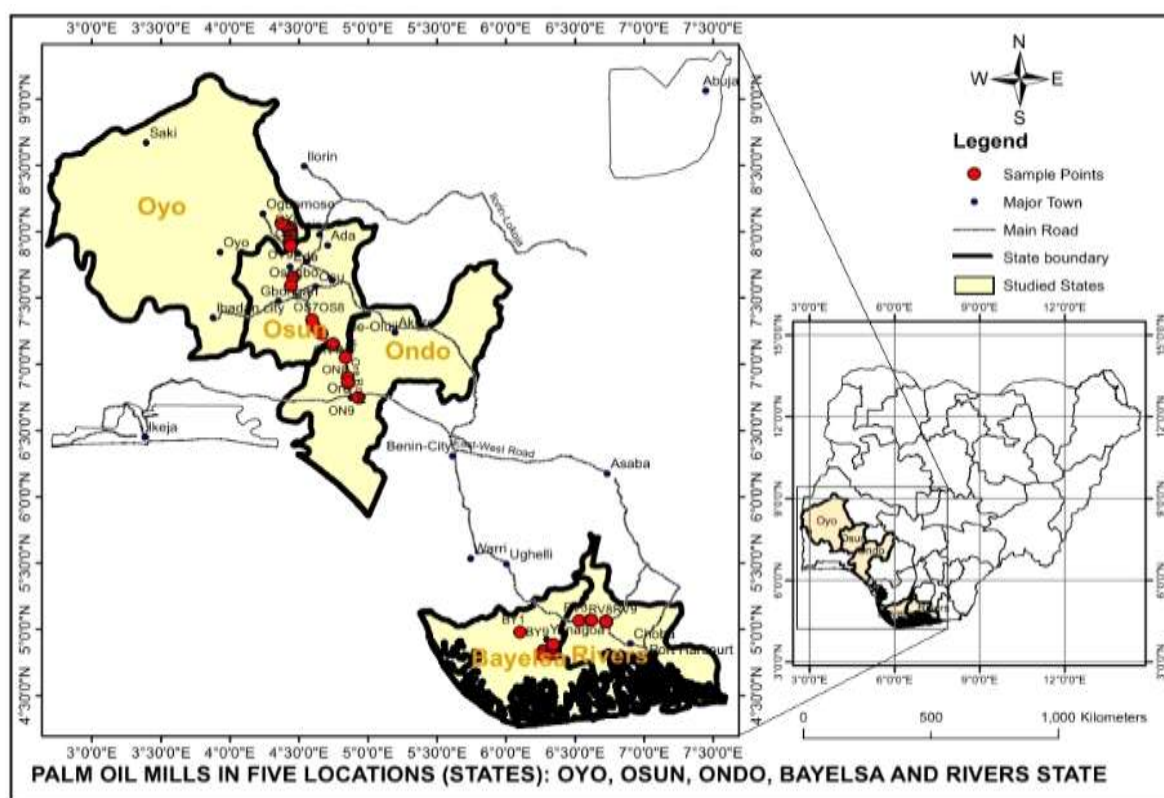


Figure1: Map of Study Area showing Sampling Sites

2.2 Elemental Analysis of Crude Palm Oil Samples

Samples were carefully handled to avoid contamination. Glassware and sample containers used were soaked in 1 M HNO₃ for 48 h and rinsed with distilled water. All reagents used were of analytical grade: 70% perchloric acid (HClO₄), 98% sulphuric acid (H₂SO₄); 69% nitric acid (HNO₃) supplied by BDH Laboratory Supplies, Poole, England. Working standards of Cd, Pb, Ni, Cr, Cu, Al, Fe, Mn, As, Zn, Ca, Mg, K, and Na were prepared by diluting concentrated stock solution (BDH Laboratory Supplies, Poole, England) of

1000 mg/L with 0.25 mol/L nitric acid.

All crude palm oil samples were analyzed for metal after digestion with mixed acid as described in AOAC (2005) and Nnorom *et al.* (2014). A 5.0 g portion of each sample was carefully weighed into a 250ml conical flask and 10 ml of the mixed acid (0.5N nitric acid, 1N perchloric acid and 1M sulphuric acid in volume ratio 2:1:2) respectively. The digestion was carried out in a fume hood on electrically operated hot plate at a temperature of 250°C for two and half hours to obtain a completely digested clear solution. The mixture was cooled to room temperature, made up to 50 ml with distilled water, agitated in a shaker and transferred to a set of centrifuge tubes, then centrifuged for five minutes at 5000 rev/min using a centrifuge (TDL-4 B. Bran Scientific and instrument company, England). The digested sample was then decanted and subjected to elemental analysis. The procedure of acid digestion was repeated but without the palm oil to serve as blank. The elements determined were: Ca, Mg, Na, K, Fe, Mn, Ni, Cr, Pb, Cd, Cu, As, Zn, and Al using flame atomic absorption spectrophotometer (FAAS: GBC Avanta PM A6600) following standard procedures.

III. Results And Discussion

The results obtained from the elemental analysis are as presented in Figure 3.1

Table 3.1: Concentration of metals in (mg/L) analyzed in Crude Palm Oil from South-West and South-South State, Nigeria

Element		Oyo	Osun	Ondo	Bayelsa	Rivers
Ca	Mean±SD	44.10±12.55	41.03± 13.70	47.41± 20.34	23.19± 7.78	25.75±11.09
	Ranges	28.36 to63.36	20.19to60.41	23.74to81.12	12.6to34.36	11.46 to 46.93
Mg	Mean±SD	5.48±3.66	7.08±11.70	8.28±5.35	5.145± 2.37	7.31±14.45
	Ranges	1.89 to12.32	2.15 to12.32	2.80 to 21.38	2.26to10.12	2.35 to12.6
Na	Mean±SD	8.20±4.85	8.137±3.21	13.72±8.36	6.39±4.73	7.65± 3.29
	Ranges	2.36 to 19.09	4.24to12.88	4.58 to 32.80	0.88 to 13.83	4.32 to13.21
K	Mean±SD	34.75± 10.49	34.96± 10.54	28.32±11.30	17.55± 8.56	15.65±5.87
	Ranges	18.53to53.88	20.53to50.42	10.36to50.21	5.29 to 35.83	6.86 to24.95
Fe	Mean±SD	53.19± 16.81	56.14± 22.28	41.09± 20.04	37.05± 18.37	34.49±15.69
	Ranges	27.61to80.00	25.57to83.94	15.30to72.60	18.54to75.33	12.48 to 66.71
Mn	Mean±SD	0.47± 0.32	0.80± 0.25	1.98 ± 1.33	0.38± 0.22	0.82±0.72
	Ranges	0.14 to1.04	0.42 to1.13	0.13 to 4.18	0.09 to 0.77	0.09 to2.48
Ni	Mean±SD	0.35±0.17	0.33± 0.18	0.65 ±0.42	0.41± 0.16	0.54±0.22
	Ranges	0.10 to 0.61	0.08 to0.63	0.10 to1.36	0.21 to 0.72	0.25 to1.02
Cr	Mean±SD	0.31±0.13	0.30±0.16	0.25± 0.15	0.16 ± 0.09	0.27±0.15
	Ranges	0.10 to0.51	0.09 to 0.57	0.07 to0.54	0.07 to 0.35	0.05 to0.51
Pb	Mean±SD	0.001±2.3E-19	0.001±2.3E-19	0.01±0.020	0.02±0.023	0.004±0.01
	Ranges	0.001to0.001	0.001to0.001	0.001 to 0.06	0.001 to 0.06	0.001 to 0.03
Cd	Mean±SD	0.001±2.3E-19	0.001±2.3E-19	0.009±0.02	0.03±0.07	0.001±2.3E-19
	Ranges	0.001to0.001	0.001to0.001	0.001 to 0.05	0.001 to 0.22	0.001to0.001
Cu	Mean±SD	0.79±0.99	0.33± 0.23	0.61±0.32	1.28± 2.18	0.77±0.30
	Ranges	0.12 to 2.93	0.01 to0.72	0.18 to 1.25	0.13 to7.39	0.26 to1.42
As	Mean±SD	0.001±2.3E-19	0.001±2.3E-19	0.001±2.3E-19	0.001±2.3E-19	0.001±2.3E-19
	Ranges	0.00 to0.001	0.001to0.001	0.001to0.001	0.001to0.001	0.001 to 0.001
Zn	Mean±SD	3.53±1.73	5.19 ± 3.13	6.94±3.08	4.99± 2.38	10.09±3.50
	Ranges	0.94 to 6.25	0.76 to 10.21	2.65 to 11.83	2.76 to9.40	4.22 to15.81

Al	Mean±SD	2.85±1.85	3.12± 1.64	2.79±2.23	1.18±1.33	2.02±1.34
	Ranges	0.49 to6.12	1.31 to6.34	0.33 to 6.23	0.19 to4.45	0.45 to4.51

Results are presented as Mean ±SD, Sample number (N=10)

The Na concentration ranged from 0.88 to 32.80 mg/kg. The highest mean sodium concentration of 13.72±8.36 mg/kg was found in Ondo samples, while the lowest concentration of 6.39±4.73 mg/kg was found in Bayelsa samples. The obtained result was very low compared to (115 to 533 mg/kg) reported by Nnorom *et al.* (2014). Sodium is necessary to maintain balance in physical fluid systems and is also required for the operation of nerves and muscles, but high-sodium diets are linked to a number of health problems including damage of the kidneys and increase in blood pressure which might cause hypertension (Mir-Marqués *et al.*, 2012). There are no dangers of excess intake of Na as the consumption of 5-10g/day of palm oil will expose a consumer to less than 6 mgNa/day.

Potassium content of crude palm oil samples from the five-state ranged from 5.29 to 53.88mg/kg and the mean values varies from 15.65±5.87 mg/kg (Rivers State samples) to 34.96± 10.54 mg/kg (Osun State samples) as the lowest and the highest values respectively (Figure 3.1). Potassium has been known to play an important role for disease prevention and control; it is an essential electrolyte for maintaining normal fluid balance in cells and a delicate balance of this element is reported to prevent an increase in blood pressure and maintain normal cardiac rhythm (Desideri *et al.*, 2012).

The mean magnesium concentration ranged from 5.145± 2.37 mg/kg for Bayelsa samples to 8.28±5.35 mg/kg for Ondo samples as the lowest and the highest values. The overall concentration ranged from 1.89-12.32 mg/kg. Magnesium play a vital role in the skeleton formation and its function in muscles and soft tissues, such as a co-factor of many enzymes involved in energy metabolism, protein synthesis, RNA and DNA synthesis, and maintenance of the electrical potential of nerve tissues and cell membranes (Mir-Marqués *et al.*, 2012). However, it should be noted that magnesium dietary deficiency, which is sufficient to induce pathologic changes, is rare (FAO/WHO, 2002).

The results showed that Calcium concentration range varies from 11.09-81.12 mg/kg across the five States, but Bayelsa samples had the lowest mean concentration of 23.19± 7.78 mg/kg and Ondo samples had 47.41± 20.34 mg/kg as the highest value. Calcium, amongst the macro elements determined showed the highest overall mean concentration (47.41± 20.34 mg/kg). It ranged from 23.74 to 81.12) mg/Kg followed by Na (13.72±8.36 mg/kg), K (34.96± 10.54 mg/kg) and then Mg (8.28±5.35 mg/kg) (Table 3.1). Calcium plays a vital role in neuromuscular function, many enzyme-mediated processes, blood clotting, and providing rigidity to the skeleton via phosphate salts (Mir-Marqués *et al.*, 2012).

The results of this research have shown that crude palm oil contains lead ranged from (0.001 to 0.06 mg/kg) with the mean concentration of varies from 0.001±2.3E-19 in both Oyo and Osun sample while Ondo samples, Bayelsa samples and Rivers samples had 0.01±0.02 mg/kg, 0.02±0.023 mg/kg and 0.004±0.01 mg/kg respectively while obtained result for Arsenic was below detection limit (0.001±2.3E-19) for all the fifty samples sites from the five States. Cypriano *et al.* (2008) reported (ND-1.82±0.01 µg/g (mg/kg) and ND-1.90±0.03 mg/kg) for Pb concentrations which were higher than (overall mean, 0.02±0.023; ranged, <0.001 to 0.06 mg/kg) result obtained from this study. Adepoju-Bello *et al.* (2012) and Nnorom *et al.* (2014) reported a 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, Nigeria, thus, this result compares well with the results of this study. Lead accumulates and substitute's calcium in bone tissues and the resultant effect is disruption of mineralization, alteration of compositional properties and bone formation mechanisms, as well as the gradual depletion of bone minerals (Medeiros., 2004; Gangoso., 2009). The Codex Standard for Named Vegetable Oils (210-1999) refers to lead and arsenic and the Codex Standard for Contaminants and Toxins in Food and Feed (193/1995, amended 2010) gives maximum levels of lead and arsenic of 0.1 mg/kg in crude and edible oils of palm and palm kernel including palmolein, stearin and superolein (FAO., 2002). Similarly, the EU limit for Pb contamination of fats and oils including milk fats is 0.10mg/kg (EU., 2001).

The overall mean Cd concentration in the crude palm oil samples studied was 0.064±0.020 mg/kg (data ranging from (0.001 to 0.06 mg/kg) with mean values for the various sites varying from 0.001±2.3E-19 mg/kg (Oyo, Osun and Rivers) to 0.009±0.02 mg/kg and 0.03±0.07mg/kg for (Ondo and Bayelsa). Adepoju-Bello *et al.* (2012) and Nnorom *et al.* (2014) reported a Cd concentration of (0.025-0.065 mg/kg and 0.024 to 0.089) respectively which compares relatively with the results from this study. Cd is known to exert adverse effects on brain metabolism and other severe effects such as prostate cancer, and could also cause kidney, liver, lungs, and bone damage (Desideri *et al.*, 2012). There is no European Standard for Cd in fats and oil, however, the limit for soybean is 0.2mg/kg (EU., 2001).

The mean Fe concentration ranged from 34.49±15.69 mg/kg to 56.14± 22.28 mg/kg for Rivers samples and Osun samples respectively with the individual concentrations ranging from 12.48-83.96 mg/kg. It has been recognized that adequate Fe in a diet is very imperative for diminishing the incidence of anemia (Ashraf and

Mian., 2008). The recommended Fe intake is 18 mg/day. Daily intake from palm oil is estimated at 0.33-1.16 and 0.65-2.32 mg/day on consumption of 5-10 g of palm oil in meals per day.

Cu in the analyzed crude palm oil samples investigated ranged from 0.01 to 7.38 mg/kg with mean values varying from 0.33±0.23 mg/kg for Osun samples to 1.28±2.18 mg/kg Bayelsa samples. Considering the highest Cu content of this study, the daily intake of Cu from consumption of 10 g of palm oil is about 1% (0.0738 mg/day) of the recommended daily intake of 2 mg/day. The Cu concentration of this research (overall mean 1.28± 2.18 mg/kg; range: 0.01-7.38 mg/kg) considered higher when compared with the Cu content obtained by Cypriano *et al.*, 2008 (ND - 2.67±0.04 and ND-2.55±0.06) and Nnorom *et al.*, 2014 (0.56-2.09 mg/kg).

Trivalent chromium (Cr⁺³) is an essential nutrient for man as it is involved in the glucose tolerance (Mir-Marqués *et al.*, 2012). Adequate chromium nutrition may reduce risk factors associated with cardiovascular diseases as well as diabetes mellitus, though hexavalent chromium is, in contrast, very toxic (Reilly., 2002). The mean concentration of Cr in samples from all five-states samples investigated was in the range 0.05-0.57 mg/kg and considered close to results reported by Nnorom *et al.*, (2014) who worked on palm oil samples from South-Eastern Nigeria (0.101-0.298 mg/kg) but higher than the values reported by Adepoju-Bello *et al.* (2012) (0.021-0.033 mg/kg).

The mean Manganese concentrations ranged from 8.09±1.53 (0.38±0.22 mg/kg) for Bayelsa samples to (1.98 ± 1.33 mg/kg) for Ondo samples (overall mean concentration of 1.98 ± 1.33 mg/kg; range: (0.09-4.18 mg/kg) were the obtained result for Mn is considered to be lower than (6.55-12.05 mg/kg) reported by Nnorom *et al.* (2014). The deficiency of manganese can result in severe skeletal and reproductive abnormalities in mammals while high doses of manganese produce adverse effects primarily on the lungs and on the brain (Zhu *et al.*, 2011).

Considering the highest Mn content of this study (4.18 mg/kg) the daily intake from 5-10 g of palm oil will be between 3-6% (8.2 E⁻⁴-0.0415 mg) of the recommended 2 mg/day.

The obtained result for Zn and Ni concentrations of this study as presented Figure 3.1 are range: (0.76-15.81 mg/kg) and (0.08-1.02 mg/kg) respectively with CPO samples from Osun having the lowest value and CPO samples from Rivers having the highest value respectively. Adepoju-Bello *et al.* (2012) reported a Ni concentration of 0.0435-0.068 mg/kg which is lower than the results of this study while Nnorom *et al.* (2014) also reported concentration of Zn and Ni values that ranged between (3.6-14.6 mg/kg and 0.15-0.81 mg/kg) which are considered comparable to results from this current study. Zinc plays essential roles as metallo-enzymes and as a cofactor of large number of enzymes. More so, Zhu *et al.* (2011) have confirmed that nickel toxicity at elevated level is more prominent, but trace amounts may be beneficial as an activator of some enzyme systems. The Draft East African Standard for Edible palm oil set the maximum limit of Pb, As and Ni in edible palm oil at 0.1 mg/kg.

The Aluminum concentrations in CPO ranged from (0.19-6.34 mg/kg) with samples from Bayelsa and Osun having the lowest and highest values respectively. Umar (2004) studied four Nigerian vegetable based oils (palm oil, palm kernel oil, shear butter and groundnut oil) and reported concentration ranges of 19.4-44.0 µg/g for Al; 30.0-81.0 µg/g for Ca; 11.9-60.4 µg/g for Cl; 1.43-5.96 µg/g for Cu; 7.3-28.1 µg/g for Mg; 0.47-1.69 µg/g for Mn; 17.5-72.8 µg/g for Na and 0.04-0.07 µg/g for V. Though our results for elements in this study were mostly higher than the results of Umar (2004), their daily intakes were adequate and pose no toxicological health concern

3.2 Estimated dietary intake of metals for consumption of 30.4g of crude palm oil samples from South-West and South-South, Nigeria

The daily intake of metals from CPO is estimated using the standard consumption of 30.4g of CPO per day. The estimates are as stated in Table 3.2.

Table 3.2. Estimated Daily Intakes of metals analyzed in crude palm oil samples (µg/kg bw/day)

Elements in CPO samples	Oyo State	Osun State	Ondo State	Bayelsa State	Rivers State	Ranges
Ca	4.654	4.325	4.996	2.443	2.715	2.443 to 4.996
Mg	0.575	0.748	0.872	0.543	0.770	0.543 to 0.872
Na	0.758	0.859	1.446	0.674	0.808	0.674 to 1.446
K	3.526	3.664	2.985	1.849	1.648	1.648 to 3.664
Fe	5.606	5.916	4.330	3.904	3.635	3.635 to 5.916
Mn	4.90E ⁻²	8.60E ⁻²	0.209	4.10E ⁻²	8.60E ⁻²	4.10E ⁻² to 0.209
Ni	3.30E ⁻²	3.36E ⁻²	6.80E ⁻²	4.30E ⁻²	5.60E ⁻²	3.30E ⁻² to 6.80E ⁻²
Cr	6.70E ⁻²	3.10E ⁻²	2.60E ⁻²	1.60E ⁻²	3.30E ⁻²	1.60E ⁻² to 6.70E ⁻²
Pb	1.10E ⁻⁴	1.10E ⁻⁴	1.39 E ⁻³	2.94E ⁻³	3.99 E ⁻⁴	1.10E ⁻⁴ to 3.99 E ⁻⁴
Cd	1.10E ⁻⁴	1.10E ⁻⁴	8.88 E ⁻⁴	1.28E ⁻²	1.10 E ⁻⁴	1.10E ⁻⁴ to 8.88 E ⁻⁴

Cu	8.30E ⁻²	3.41E ⁻²	6.40E ⁻²	0.134	8.20E ⁻²	3.41E ⁻² to 0.134
As	1.00E ⁻⁴	1.10E ⁻⁴	1.10E ⁻⁴	9.02E ⁻⁵	1.10 E ⁻⁴	9.02E ⁻⁵ to 1.10 E ⁻⁴
Zn	3.63E ⁻¹	0.549	0.732	0.526	1.062	3.63 E ⁻¹ to 1.062
Al	3.00E ⁻⁴	0.329	0.292	0.123	0.212	3.00E ⁻⁴ to 0.329

Results are presented as Mean, Number of Samples per State, N=10

The estimated dietary intakes for Calcium and Magnesium obtained (Table 3.2) ranged from (2.443 to 4.996 μg/kg bw/day) and (0.543 to 0.872 μg/kg bw/day) with the consumption 30.4kg or 11g of crude palm oil and these values were considered moderate compared to what Nnorom *et al.* (2014) reported (0.73-3.43 μg/kg bw/day and 1.45-6.86 μg/kg bw/day) considering the consumption of 5g and 10g of fresh palm oil in meals. The recommended dietary allowance (RDA) for Calcium (Ca) is set at 1000 mg Ca/day while Magnesium (Mg) for male and female healthy adults are 400–420 and 310–320 mg Mg/day respectively (Institute of Medicine, 2002).

The estimated daily intake of potassium and Sodium in this study ranged from (1.648 to 3.664 μg/kg bw/day and 0.674 to 1.446) μg/kg bw/day, which is very low compared to the recommended K intake of 1000 mg/day. Meanwhile, Nnorom *et al.* (2014) reported a very low Daily intake of K from consumption of 5g and 10g of fresh palm oil (0.39 and 1.65 μg/kg bw/day).

Fe and Mn estimated dietary intake from this study at consumption of 30.4g/kg crude palm oil samples varied from (3.635 to 5.916 μg/kg bw/day) and (0.041 to 0.209 μg/kg bw/day) for Fe and Mn, respectively. The intake values of Fe and Mn were less than the recommended dietary allowance value for Fe and Mn. It has been recognized that adequate Fe in a diet is very imperative for diminishing the incidence of anemia (Ashraf and Mian., 2008). Nnorom *et al.* (2014) reported a very low estimated daily intake of 0.33-1.16 and 0.65-2.32 mg/day on consumption of 5-10 g of palm oil in meals per day while the recommended Fe and Mn intake is 10-18 mg/day person and 2–5 mg/day person.

The estimated daily intake of Ni ranged from 3.30E⁻² to 6.80E⁻² μg/kg bw/day. The tolerable daily intake of Ni is 1.0 μg/kg bw/day (Institute of Medicine, 2010).

In this study, the highest dietary intake of Cr⁺³ was obtained from the consumption of crude palm oil (1.60E⁻² to 6.70E⁻² μg/kg bw/day) while lower intakes of Cr were obtained from Bayelsa and Oyo samples. These values were lower than the values reported by Adepoju-Bello *et al.* (2012) and Nnorom *et al.* (2014). The recommended dietary allowance of Cr is equivalent to 2.2 mg/kg bw/day (Institute of Medicine, 2010).

The Cadmium estimated daily intake from the consumption of these CPO spanned between 0.00011 to 0.000888 mg/kg bw/day. The tolerable intake value of Cd is set at 1 mg/kg bw/day (WHO 1993).

The estimated intake values of Lead (Pb) in this study ranged (0.00011 to 0.000399 μg/kg bw/day) was found below recommended values of 0.1 μg/kg bw/day.

The recommended dietary allowance (RDA) for Cu ranged from 15–500 μg/kg bw/day (World Health Organization (WHO) 1993). The estimated daily intake value for Cu in this study ranged from 0.04 to 2.50 μg/kg bw/day, while that of Arsenic ranged from 9.02E⁻⁵ to 1.10 E⁻⁴ μg/kg bw/day (which was below detection limit of the AAS used in this study). Arsenic has no biological function in humans although animal data indicate a requirement, no data on the possible adverse effects of organic arsenic compounds in food were found, however, inorganic arsenic is a known toxic substance.

The Joint FAO/WHO Expert Committee on Food Additives (JECFA) provisional maximal tolerable daily intake of Zn is 1000 μg/kg bw/day (World Health Organization (WHO), 1982) while the Expert Group on Vitamins and Minerals (EVM) safe upper limit (SUL) for Zn is 4.2 mg/day (equivalent to 700 μg/kg bw/day in a 60 kg adult) for total dietary intake (EVM, 2003). The estimated intakes of Zn from the consumption of these CPO samples from the five states ranged from 3.63 E⁻¹ to 1.062 μg/kg bw/day. The highest intake value was obtained from consumption of CPO samples from Rivers. The estimated intake values of Zn in this study were less than 9.7e⁻⁴% of the provisional maximal tolerable daily intake of Zn at 11 μg/kg bw/day 60kg adult.

Lastly, the estimated dietary intake for Aluminum in this study ranged from 3.00E⁻⁴ to 0.329 μg/kg bw/day. The results of the estimated dietary intakes of the metals analyzed in the crude palm oil were all below recommended values.

3.3 Estimation of Target Hazard Quotients

In order to determine the level of concern arising from metal concentration, Target Hazard Quotient (THQ) values were calculated using the measured metal concentration in the intact samples for ten potentially toxic metals in the crude palm oil samples. The THQ is a ratio between the measured concentrations and the oral reference dose, weighted by the length and frequency of exposure, amount ingested of samples, and body weight (Hague *et al.*, 2008). The THQ is calculated by Equation 1, the formula established by the Environmental Protection Agency (USEPA 1989) using equation (1).

$$THQ = \frac{E_F \times E_D \times SF_R \times MCS_{inorg} \times C_F}{R_F D \times W_{AB} \times T_A} \quad \text{Equation 1}$$

where THQ is the Estimated Target Quotients

E_F - the exposure frequency (365 day/years)

E_D , the exposure duration equivalent to life time (54-56 life expectancy for Nigeria, and the mean value of 55.20 years was used)

SF_R - the fresh food ingestion rate (g/person) which was considered to be 30.4 g/day for palm oil;

C_F - the conversion factor (10^{-3}) for fresh weight

MCS inorg- the concentration of inorganic species in dietary components (mg/kg wet weight) for each element determined in food stuff.

W_{AB} - the average body weight (bw) (average adult body weight was considered to be 60kg)

AT_n - the average exposure time for non-carcinogen ($E_F * E_D$)

R_{FD} = Reference Oral Dose (for Cr = 1.5×10^{-3} , Cu = 4.0×10^{-2} , Zn = 3.0×10^{-1} , Fe = 7.0×10^{-1} , Ni = 2.0×10^{-2} , Mn = 1.4×10^{-1} , Pb = 1.5, Cd = 1.0×10^{-3} , Al = 1.2×10^{-1} and As = 3×10^{-4})

Estimation of dietary intakes of metals, with ingestion rate of 30.4g/day of crude palm oil sample, was used as standard. For this study, the length of exposure was set to 13789 days for Nigeria based on the average life expectancy of 55.20 years, from 15 years of age (World Health Organization (WHO), 2004; Statista, 2018). The average weight of 60 kg adult was adopted in this study. The estimated THQ values (Table 3.3) for individual metals from consumption of one 30.4g per day was less than one in all the crude palm oil samples from all the five States.

Table 3.3 Estimation of target hazard quotients of heavy metals in crude palm oil samples from South-West and South-South, Nigeria.

Sample site	Fe	Mn	Ni	Cr	Pb	Cd	Cu	As	Zn	Al	Combine THQ
Oyo	2.15E-2	9.60E-3	4.88E-3	5.88E-2	1.90E-7	2.80E-4	5.32E-3	9.40E-4	1.90E-3	6.63E-03	9.90E-02
Osun	2.26E-2	1.65E-3	4.62E-3	5.59E-2	1.90E-7	2.80E-4	2.30E-3	9.40E-4	5.55E-3	7.34E-03	1.01E-01
Ondo	1.67E-2	3.93E-3	9.18E-3	4.65E-2	1.82E-6	2.72E-3	4.35E-3	9.40E-4	6.55E-3	6.58E-03	9.75E-02
Bayelsa	1.49E-2	7.73E-3	5.35E-3	3.03E-2	3.85E-6	8.65E-3	9.06E-3	9.40E-4	4.70E-3	4.25E-03	7.89E-02
Rivers	1.48E-2	1.60E-3	1.25E-3	5.10E-2	7.91E-7	2.80E-4	6.06E-3	9.40E-4	9.50E-3	4.70E-03	9.83E-02

Results are presented as Means, Number of Samples per State, N=10

The THQ values <1 indicate safe level while THQ values >1 indicate levels of concerns. THQ values are additive not multiplicative, thus a THQ value of 20 is larger but not 10-fold greater than a THQ = 2. The combined THQ values for crude palm oil analyzed were <1. From the estimated THQ values, no lifelong health concern of metals is associated with the consumption of these locally produced crude palm oil samples from the five States studied.

3.4 Health Risk Index due to intake of metal contaminated crude palm oil

The Health risk of consumer due to intake of metal contaminated palm oil or food/fish was assessed by using HRI

$$HRI = (EDI/R_{FD}) \times 10^{-3}$$

Where EDI = estimated daily intakes

R_{FD} = Reference Oral Dose (for Cr = 1.5×10^{-3} , Cu = 4.0×10^{-2} , Zn = 3.0×10^{-1} , Fe = 7.0×10^{-1} , Ni = 2.0×10^{-2} , Mn = 1.4×10^{-1} , Pb = 1.5, Cd = 1.0×10^{-3} , Al = 1.2×10^{-1} and As = 3×10^{-4})

The result of health risk assessments (HRI) of the various heavy metals considered in this study are presented in Table 3.4.

Table 3.4. The Health risk index of consumer due to intake of metal contaminated crude palm oil samples from South-West and South-South, Nigeria.

Sample sites	Fe	Mn	Ni	Cr	Pb	Cd	Cu	As	Zn	Al
Oyo	7.89E-3	3.22E-3	1.65E-3	2.25E-2	7.30E-8	1.10E-4	2.10E-3	3.70E-5	1.20E-3	2.51E-3
Osun	8.17E-3	1.07E-3	1.41E-3	2.06E-2	7.30E-8	1.10E-4	8.38E-4	3.70E-4	2.90E-3	2.75E-3
Ondo	6.16E-3	1.49E-3	3.40E-3	1.70E-2	9.28E-7	8.88E-4	1.62E-3	3.70E-4	2.44E-3	2.44E-3
Bayelsa	5.56E-3	2.92E-3	2.15E-3	1.07E-2	1.97E-6	1.21E-2	3.41E-3	3.03E-4	2.76E-3	1.03E-3
Rivers	5.18E-3	1.14E-3	3.05E-3	2.19E-2	2.66E-7	1.10E-4	2.75E-3	3.70E-3	3.54E-3	5.32E-3

Results are presented as Means, Number of Samples per State, N=10

The results indicate that there is no HRI value > 1, indicating that humans would not experience any

significant health risk if they only consume metals from these crude palm oil samples from South-West and South-South local palm oil mills, in Nigeria. Among the heavy metals examined in this study were Pb, Cd and As with a HRI value ranged between ($7.30E^{-8}$ to $1.97E^{-6}$) for Pb, ($1.10E^{-4}$ to $1.21E^{-2}$) for Cd and As ($3.70E^{-5}$ to $3.70E^{-3}$) with relatively low potential health risk, while Cd (HRI = $1.21E^{-2}$ from Bayelsa) has the highest potential health risk.

Reports have it that exposure to more than one contaminant may produce an adverse effect on the consumers. In this study, the total HRIs of the individual metals examined in the crude palm oil samples was calculated by adding the individual HRIs of the metals. The total HRI through the consumption of CPO was less than 1, indicating that there is no potential significant health risk associated with the consumption of CPO from the five States. The CPO samples from Bayelsa which its Cd was the major health risk contributors, accounted for 23% of the total HRIs in the study.

IV. Conclusion And Recommendation

Generally, this study has shown that the palm oils from the studied areas do not pose any health risk from toxic heavy metals including Cd, Pb, As and Al as the concentrations were generally low but would rather act as a source of both macro and micronutrients in diets. The mean concentrations of the metals were lower than recommended values by the EU, WHO and EVM. The samples vary widely in their heavy metal contents, but the estimated daily intake of the various metals in the samples were below their respectively recommended limits. From the health point of view, the THQ and HRI values for the individual metals showed that there was no health risk for humans due to the intake of individual heavy metals in the crude palm oil from the South-West and South-South, Nigeria. Also, the THQ and total HRI on humans due to the combined effect of all the metals considered in the study was also less than one, which indicate that potential health risk for consumption of the crude palm oil is insignificant.

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