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Comparative study of trace metal (Cd, Cr, Cu, Fe, K, Mg, Na, and Zn) contents of local and imported vegetable oil brands consumed in Nigeria

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ABSTRACT

This paper reports the results of the study of Cd, Cr, Cu, Fe, K, Mg, Na, and Zn contents of 20 branded vegetable oil (10 local and 10 foreign brands) samples purchased from markets in Abia State, South-eastern Nigeria. The metals were determined using atomic absorption spectrophotometer after acid digestion. The metals (mg/kg) determined for local brands of vegetable oil varied as follows: 64.2-443 for Na; 0.005-101 for K; 12.9-222 for Mg; ND-1.8 for Cr; 0.22-4.99 for Cu; 50-425 for Fe and 9.1-25 for Zn. For the foreign brands, the concentration (mg/kg) varied from 113-452 for Na; 0.002-103 for K; 46-177 for Mg; 0.015-1.67 for Cr; 0.69-3.44 for Cu; 125-413 for Fe and 9.1-31.8 for Zn. The Cd contents were generally below detection limit and only two foreign brands had detectable Cd concentrations (0.012 and 0.602 mg/kg). On the overall, iron concentration was higher than other trace metals in the examined vegetable oils. Apart from Cd content, the metals concentrations of investigated local brands of vegetable oil compared well with their foreign counterparts. The results of this study showed that the estimated intake levels for these metals, when compared with set safety levels, should pose no risk to human health.

Key words: Micronutrient, heavy metals, vegetable oil, Nigeria,

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INTRODUCTION

Oils and fats supply an average 15–30% of a man's daily calories need and they are important source of energy in the human diet [1]. The oil compositions differ depending on the vegetal species from which they are obtained; and even within the same species, the content and composition of these components can vary due to the agronomic and climatic conditions, fruit or seed quality, oil extraction system and refining procedures [2]. Vegetable oils and fats are composed basically of triglyceride and fatty acids. The triacyl glycerols (95–98%) are the major components with constituents composed of complex mixture of minor compounds (2–5%) of a wide range of chemical nature and metals [2]. They can be produced from seeds of different plants, such as: castor bean, corn, cotton seed, curcas bean, fodder turnip, palm fruit, sunflower seed, soybean, tung, among others [3]. Other vegetable sources such as groundnut, rapeseed, safflower, sesame, coconut, mustard, rice bran, watermelon, neem, mahuwa etc. are also used as raw material sources in vegetable oil manufacture [4]. The varying sources of vegetable oils indicate that there would be differences in the composition of the finished product especially with respect to fatty acid compositions, degree of saturation, among others.

Industrial operations are usually applied in processing natural vegetable oil to remove the components which may impact negatively on the desirable qualities of the finished product such as appearance, taste, stability, or nutritional value.

Cert and co-workers observed that during storage of the oil, chemical processes such as hydrolysis, esterification and oxidation introduce change in the minor constituents. Consequently, they are of the opinion that the determination of the minor constituents of vegetable oil is essential for the analytical assessment of the quality, origin, extraction method, refining procedure and possible adulteration of the vegetable oils [2].

Being of natural sources, vegetable oil contains trace amounts of metals, which at higher concentrations increase the oxidation rate of oil. Metals present in vegetable oils can be from mineral uptake from the soil on which the plant is grown as well as from other sources such as the application of agrochemicals like fertilizers and pesticides [5]. The use of metal equipment in the production processes, storage and transportation could contribute to the metal contamination, thereby constituting source of metals contained in the finished products.

Many metals are beneficial to humans but their levels in foods are of significant interest because, above certain levels, they may become harmful. Consequently, it is important to ascertain the levels of both beneficial and toxic metals in foods, and such information is imperative in estimating dietary intakes of such metals. The Global Environment Monitoring System - Food Contamination Monitoring and Assessment Programme (GEMS/Food) of the World Health Organization (WHO) encourages studies of total diet as a means of evaluating food contamination of chemicals and by extension, human intake of such chemicals around the world [6].

In recent times, there have been an increasing number of publications on the trace elements contents of food and foodstuff, especially with the enhanced awareness on the role of trace elements in human health [7–9]. Increasing numbers of publications have reported the deleterious effects that trace metals have on the flavour and oxidative stability of oils, since some metals could catalyse oxidation of fatty acid chains, exerting a deleterious influence on shelf life and nutritional value [10, 11]. However, there is a dearth of data from Nigeria.

Metal elements such as Na, K, Mg, Cu, Cr, Fe and Zn are essential nutrients for human growth. Nevertheless, certain metals (Cd and Pb) can also be toxic, even in relatively little concentration and therefore pose risk to human health [12]. Vegetable oils are widely used in cooking and food processing, cosmetics, pharmaceutical and chemical industries [13]; thus, ascertaining their metal contents is germane. This is because the presence of toxic metals such as Pb and Cd could have undesirable health consequences. To protect human, the Joint FAO/WHO Expert Committee on Food Additives (JECFA) set a provisional tolerable weekly intake (PTWI) for Cd at 7 µg/kg body weight (equivalent to 1 µg /kg bw per day) [14, 15]. Similarly, a tolerable weekly intake (TWI) of 2.5 µg /kg bw (equivalent to 0.36 µg/kg bw per day) of Cd was established by EFSA [16]. For Pb, an acceptable daily intake for adults was set at between 0.21 and 0.25 mg per day, (or between 1.5 and 1.75 mg per week) [17].

This study is part of a comprehensive investigation into the metal contents of consumer products marketed in Nigeria to understand contamination status, spatial similarities/differences, and possible human intake rates of the metals by consumers. The aim of this paper therefore, is to characterize edible oil (foreign and local) in terms of trace metal content and compare our results with literature and set standards for foods. Our study is of considerable interest considering that these oils are consumed in large quantities in Nigeria. The level of Cd, Cr, Cu, Fe, K, Mg, Na, and Zn of some edible vegetable oils from Nigeria markets was investigated and the outcome of this study provides additional information, which is vital in evaluating the nutritional benefits and the likely toxicological implications of the consumption of foods prepared with these oils.

MATERIALS AND METHODS

Sampling

Twenty (20) samples of edible vegetable oil (10 local brands and 10 foreign brands) marketed in southeastern Nigeria were purchased and investigated for their metal contents. The samples were purchased between December 2012 and January 2013. The brands studied include Lion King, Sous, Envoy, Laser, First Choice, Diamond, Ideal, Solive, Gold, Twin Lion, Star Arrival, Kings, Grand, Baron, Fresh, Ok, Lahda, Life, Vikings and Turkey, which were presented using 'sample codes'.

Sample analysis

All samples were analyzed as purchased without any further pre-treatment. 1 g of the sample was weighed accurately and transferred into a 250 mL conical flask. 10 mL of the acid digestion mixture (Perchloric, Nitric and Sulphuric acid in the ratio of 1:2:2) was added into 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 filtered using ashless Whatman filter into a 100 mL volumetric flask and made to mark with distilled water. The digests were subsequently analyzed for Cd, Cr, Cu, Fe, K, Mg, Na, and Zn using Phoenix 986 (Biotech Engineering Management Co. Ltd. UK) flame atomic absorption spectrophotometer.

Statistical analysis

Statistical analysis of data was treated using Excel 2007 statistical package program. Unpaired Student's *t*-test was employed to determine whether significant differences existed between metal contents of foreign and local brands of the vegetable oils. The significance was set at 0.05, and *t* Stat value was compared with corresponding *t* Critical two-tail value. When the *t* Stat value was less than the *t* Critical two-tail value, conclusion was reached that there was no significant difference between the two brands of vegetable oil.

Quality assurance

All chemicals used were of analytical grade: $HClO_4$ (70%, Sigma-Aldrich, St. Louis, USA), H_2SO_4 (98%, BDH Laboratory Supplies, Poole, England); HNO_3 (69%, BDH Laboratory Supplies, Poole, England). All plastics and glassware were carefully cleaned by washing, rinsing severally with tap water before soaking in 5% HNO_3 solution for a minimum of 24 h to eliminate the risk of contamination during the experiments. They were rinsed severally with deionized water before use. Reagent blank determinations were used to correct the instrument readings. Report has it that the slopes of the calibration curves obtained using either inorganic or organic standards are very similar when dealing with vegetable oils, thus, their trace metals content can be determined through external calibration technique, using either inorganic or organic standards [11]. Therefore, the accuracy of the analytical method was verified by analyzing a certified reference material (Accu Standards, New Haven, USA) as well as conducting spike recovery on some of the samples. Detection limit was defined as the concentration corresponding to three times the standard deviation of seven blanks. Recoveries for the spiking study and CRM analysis ranged from 98.3 – 100.2 % and 99.2 – 100.8 % respectively (Tables 1 and 2).

Table 1. Elements concentration in certified reference material (Accu standard USA)

Element	Certified value (mg/L)	Determined value (mg/L)	Recovery (%)
Na	3.00±0.42	2.98±0.71[a]	99.3
Zn	0.250±0.031	0.249±0.104	99.6
Cr	0.0625±0.0241	0.063±0.0210	100.8
K	5.00±0.06	4.997±1.075	99.9
Fe	0.125±0.042	0.124±0.021	99.2
Mg	1.00±0.02	0.997±0.063	99.7

[a] *Mean ±standard deviation (n = 3)*

Table 2. Recoveries for some spiked vegetable oil samples

Elements	Sample ID	Spiked Concentration (mg/kg)	Recovered Concentration (mg/kg)	Recovery (%)
Fe	TI-27	175±2[a]	175.3±2.5	100.2
	IA-14	145±1	144.7±1.4	99.8
Mg	SU-11	16.9±1.2	16.8±2.8	99.4
	DI-21	67.9±1.5	67.1±4.1	98.8
Na	VI-28	272.2±0.4	271.9±1.7	99.9
	DA-13	64.2±1.1	63.9±2.1	99.5
Cu	FO-15	3.0±0.4	2.95±0.25	98.3
	SO-19	2.5±0.3	2.46±1.01	98.4
Zn	LO-20	13.6±0.7	13.57±0.23	99.8
	EO-10	12.7±0.4	12.69±1.04	99.9
K	BA-18	0.008±0.010	0.008±0.031	100.0
	FE-12	70±2	69.84±1.21	99.8

[a]*Mean ±standard deviation*

Estimation of daily Intake of metals from the vegetable oil brands studied

Zhu and co-workers estimated the dietary intakes of eight heavy metals from weekly consumption of 175 g of edible vegetable oils or daily consumption of 25 g of edible vegetable oils for a 70 kg individual, and reported that consumption of such quantities should pose no risk to human health [18]. Considering that in Nigeria, vegetable oils are most often, not consumed directly– they are either used in food processing or other products– 25 g would suffice to estimate the daily intake of the metals for both the local and foreign brands. The values obtained were compared with their corresponding recommended daily intakes (RDI) and recommended dietary allowances (RDA).

RESULTS AND DISCUSSION

Elemental concentration of local and foreign brands of vegetable oil

The metal contents of the individual foreign and local brands of vegetable oil studied were presented in Table 3. The summary of results and comparison of the Cu, Fe, K, Mg, Na, and Zn contents of the foreign and local brands were presented in Figure 1. Sodium and iron concentrations in both local and foreign brands were high (Figure 1). The lowest concentration of Na in foreign brands of vegetable oil was 113 mg/kg while the highest concentration was 452 mg/kg. The minimum concentration obtained for local brands was 64.2 mg/kg whereas the maximum was 443 mg/kg. Sodium is necessary to maintain balance in physical fluid systems and is also required for the operation of nerves and muscles. However, high-sodium diets are linked to a number of health problems including damage of the kidneys and increase in the possibilities of hypertension [19]. Consequently the Na contents of the samples investigated will not pose health risks since vegetable oils are not consumed directly, but used in almost all foods processing.

The minimum Fe concentrations for foreign and local brands were 125 and 50 mg/kg respectively. Fe in a diet is very imperative for diminishing the incidence of anemia [20]. The Fe contents of vegetable oils in this study (236±99 mg/kg) were higher than values reported by several authors, which ranged from 0 to 220 mg/kg (Table 4); but were adequate as their intakes were below their corresponding limits. The maximum Fe concentrations of 413 and 425 mg/kg were determined in foreign and local brands respectively.

The K concentrations of both foreign and local brands were generally low. Local and foreign brands had 0.005 and 0.002 mg/kg respectively as their minimum K concentration, while their maximum concentrations were 101 and 103 mg/kg respectively. Potassium 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 [21]. Mg was also present at concentrations of 46 – 177 mg/kg and 12.9 – 222 mg/kg in foreign and local brands respectively.

Among other essential micro elements studied, the trend in concentration was Cr<Cu≪Zn. Chromium was not detectable in most foreign and local brands analyzed. This was consonant with the values (0.0005±0.0001 – 0.0010±0.0001 mg/kg) obtained by Pehlivan and co-workers on edible vegetable oils in Turkey [12]. However, brands in which they were detectable, contained as much as 0.015 – 1.67 mg/kg and 0.74 – 1.8 mg/kg in foreign and local brands respectively (Table 3). Though trivalent chromium is an essential nutrient for humans, which is involved in the glucose tolerance [19]; the level of Cr in these samples calls for health concern. Going by the observation that Cr was not detectable in some brands, processing methods could be the culprit for the high levels in some brands. Adequate chromium nutrition may reduce risk factors associated with cardiovascular disease as well as diabetes mellitus, though hexavalent chromium, in contrast, is extremely toxic [22].

Copper and zinc are required in our diet because they exhibit a wide range of biological functions such as components of enzymatic and redox systems [24]. Copper concentrations in this study ranged from 0.69 – 3.44 mg/kg in foreign brands to 0.22 – 4.99 mg/kg in local brands. Cu Concentrations of the present study were higher than the recommended value [24], but is also comparable to the results of previous studies (Table 4).

Zinc concentrations of our study ranged between 9.1 – 31.8 mg/kg in foreign brands and 9.1 – 15.9 mg/kg in local brands. The Zn levels in the investigated oil samples were higher than those of the literature values presented in Table 4.

Cadmium is known as a principal toxic element, since it inhibits many life processes [25, 26]. It can be taken up directly from water, and to some extent, from air and through food, and it has a tendency to accumulate in both plants and animals [12]. Cadmium concentrations were below the detection limit in all of the local brands of vegetable oil and most of the foreign brands: Cd was detected in two foreign brands at 0.012 and 0.602 mg/kg levels (Table 3). This corroborated the reports of Pehlivan and co-workers that reported Cd concentrations of

0.0007±0.0002 – 0.0045±0.0002 mg/kg in edible vegetable oils in Turkey [12]. Other literature values presented in Table 4 were all lower than the value of the present study.

Table 3. Metals concentration of different brands of vegetable oil (mg/kg)

Sample ID	Brand	Na	K	Mg	Cd	Cr	Cu	Fe	Zn
LO-20	*Foreign*	267	0.003	81.9	ND	ND	3.29	225	13.6
SU-11	*Local*	77.6	0.005	16.9	ND	ND	0.22	50.0	9.10
EO-10	*Local*	323	19.5	83.9	ND	ND	4.18	250	12.7
LE-22	*Foreign*	452	103	177	ND	ND	2.99	288	25.0
FO-15	*Local*	175	7.79	36.9	ND	ND	2.99	250	13.6
DI-21	*Foreign*	255	1.95	67.9	0.012	0.61	3.44	250	20.5
IA-14	*Local*	116	0.009	27.9	ND	0.74	1.39	145	9.10
SO-19	*Local*	170	0.005	33.9	ND	1.80	2.48	313	11.4
GO-23	*Foreign*	125	0.006	63.9	ND	ND	1.11	325	15.9
TI-27	*Foreign*	167	0.006	74.9	ND	ND	0.99	175	13.6
SA-17	*Local*	443	101	222	ND	ND	1.66	425	25.0
KI-25	*Foreign*	240	0.008	62.9	ND	ND	1.24	288	15.9
GA-16	*Local*	138	0.005	54.9	ND	ND	4.99	125	15.9
BA-18	*Local*	140	0.008	45.9	ND	ND	2.24	188	11.4
FE-12	*Local*	123	70.0	24.9	ND	ND	1.33	150	13.6
OK-29	*Foreign*	153	0.002	59.9	ND	ND	0.69	125	9.10
DA-13	*Local*	64.2	0.009	12.9	ND	ND	1.20	200	13.6
LI-26	*Foreign*	257	0.016	70.9	ND	ND	0.97	413	18.2
VI-28	*Foreign*	272	33.1	64.9	0.602	1.67	1.28	350	31.8
TU-24	*Foreign*	113	11.2	46.0	ND	0.015	1.51	189	26.8

ND- Not Detected; Instrument Detection limit is 0.001mg/kg

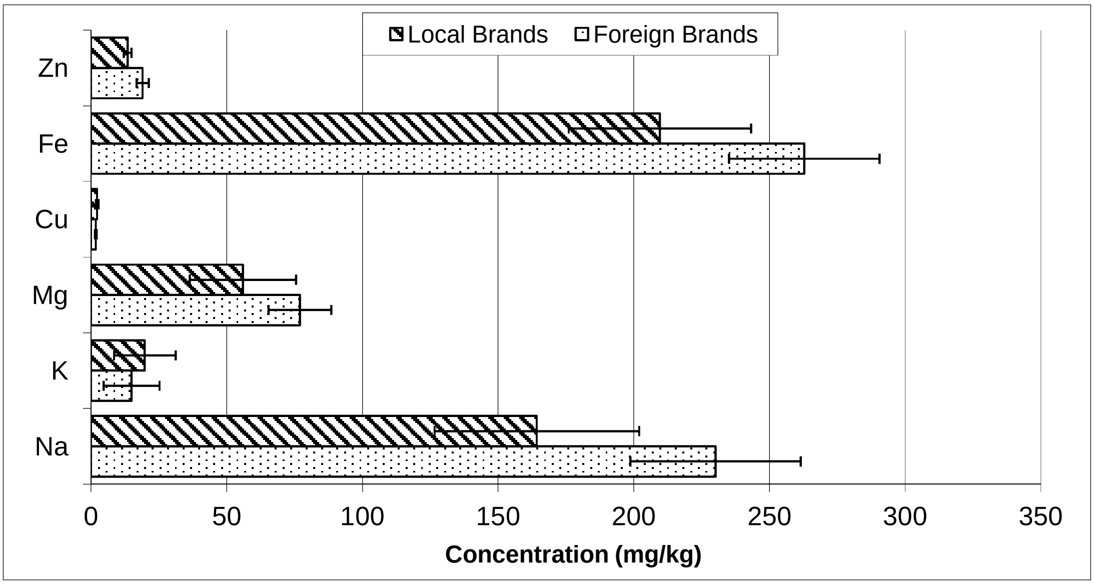

Figure 1. Mean concentration of some elements in foreign and local brands of vegetable oils

Unpaired Student's *t*-test showed that mean values ($t_{exp}<t_{crit}$; 2.09<2.13, *n*=10, *P*=0.05 for Zn; 1.22<2.11, *n*=10, *P*=0.24 for Fe; 0.91<2.12, *n*=10, *P*=0.38 for Cu; 0.93<2.13, *n*=10, *P*=0.37 for Mg; 0.32<2.10, *n*=10, *P*=0.75 for K and 1.09<2.10, *n*=10, *P*=0.29 for Na) did not significantly differ.

Correlations studies showed strong association between the metals in the local brands compared to the foreign brands (r>0.6 was accepted as strong). For instance Na/K (0.68); Na/Mg (0.93); Na/Fe (0.81); Na/Zn (0.75); K/Mg (0.75); K/Zn (0.78); Mg/Fe (0.75); Mg/Fe (0.88); Fe/Zn (0.70) were correlated for local brands. For the foreign brands, the following were strongly correlated: Na/K (0.79); Na/Mg (0.86); K/Mg (0.89).

Estimation of Intake of nutritional elements and potentially toxic metals

Results of the estimated intake of metals have revealed that both local and foreign brands of vegetable oils can furnish consumer with essential minerals without any attendant health effect. Daily consumption of 25 g of foreign brands of vegetable oil will furnish the body with 2.8 – 11.3 mg of Na, 0.00001 – 2.6 mg of K, and 1.2 – 4.4 mg of Mg; while same quantity of local brands will provide the body with 1.6 –11.1 mg of Na, 0.00001 – 2.5 mg of K and 0.3 –5.6 mg of Mg. The minimum daily requirement of Na is 1500 mg, while the maximum recommended intake is 2400 mg per day [27, 28]. The estimated intake was in no way close to the recommended intake as it will take the consumption of about 3.32 – 13.3 kg or 5.31 – 21.3 kg of either brands of vegetable oil to exceed the minimum or maximum limits respectively. The recommended daily intake of K according to FAO/WHO is 4700 mg daily [30]. Thus, the daily intake of foreign or local brands of vegetable oil posed no threat to potassium toxicity. Also, daily Mg intake was well below the recommended dietary allowance set by Food and Nutrition Board, which is 350 mg per day [27]; and consumers may require taking about 2 – 8 kg of either brands of vegetable oil to exceed this limit.

The estimated daily intakes of some of the essential micro elements were below their corresponding recommended dietary allowances, which are 0.9 and 18 mg/day for Cu and Fe respectively; and adequate intake of 11 mg/day for Zn [30]. Daily consumption of 25 g of either local or foreign brands of vegetable oil will provide the consumer with 0.006 – 0.12 or 0.02 – 0.09 mg of Cu, 1.25 – 10.6 or 3.12 – 10.3 mg of Fe and 0.23 – 0.4 or 0.23 – 0.8 mg of Zn respectively. The daily intake of Cr ranged from 0 – 0.05 mg from the consumption of 25 g of foreign brands and 0 – 0.04 mg from the consumption of same quantity of local brands. Adequate intake of Cr as stipulated by Food and Nutrition Board is 0.03 mg/day [29]; therefore, consumers may consider limiting their vegetable oil intakes to 17 g in order not to exceed the limit.

Cd was not detected in local brands of vegetable oil, while some foreign brands contain little amount of Cd (Table 3). The daily intake estimated from the consumption of 25 g of foreign brands was 0.02 mg. The RDI for Cd is 0.07mg [30]; thus it will only take the consumption of about 120 g of foreign vegetable oil to be exposed to Cd toxicity.

Table 4. Comparison of trace metals contents of vegetable oils

Element	Concentration (mg/kg)	Reference
Fe	<2.1 – 3.13	[11]
	0.0039 – 0.0352	[12]
	16.2 – 45.3	[18]
	0.22 – 220	[32]
	52.0 – 291.0	[33]
	0.0 – 0.8	[34, 35]
	50 – 425	**Present study**
	1.0 – 1.5	Recommended value [24]
Zn	0.00273 – 0.00769	[5]
	<0.4 – 4.61	[11]
	0.0184 – 0.2870	[12]
	0.0255 – 0.6617	[13]
	0.742 – 2.560	[18]
	0.04 – 0.70	[32]
	9.10 – 31.80	**Present study**
	NA	Recommended value [24]
Cu	<0.40 – 1.33	[11]
	0.0184 – 0.2870	[12]
	0.027 – 0.854	[13]
	0.021 – 0.265	[18]
	0.02 – 0.33	[32]
	0.000 – 0.130	[34, 35]
	12.71 – 50.50	[36]
	21.0 – 31.0	[37]
	0.22 – 4.99	**Present study**
	0.1	Recommended value [24]
Cd	0.0017 – 0.00618	[5]
	0.0007 – 0.0045	[12]
	0.00051 – 0.00672	[13]
	0.00264 – 0.00843	[18]
	ND – 0.602	**Present study**
	0.05	Recommended value [24]

NA- Data not available

CONCLUSION

This study contributes new data on the trace elements content of some branded vegetable oil samples marketed in southeastern Nigeria. In the present study, very low concentrations of toxic metal Cd was observed in branded vegetable oil samples with a range of 'not detected' to 0.602 mg/kg. Local brands of vegetable oil should be encouraged and patronized having shown undetectable levels of the studied toxic metals, and containing adequate essential elements needed by human. The vegetable oil brands investigated contained high amounts of Fe, Na and Mg with ranges of 50–425 mg/kg, 64.2–452 mg/kg, and 16.9–222 mg/kg respectively. The cadmium contents were generally below the 0.05 mg/kg limits. The results of this study provide detailed information on the micronutrient benefits of foods prepared with the vegetable oil brands marketed in Nigeria. The results also show that there is no toxicological health risk from Cd in the use of the studied brands of vegetable oil in food preparation.

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