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Human dietary exposure to metals in the Niger delta region, Nigeria: Health risk assessment

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ABSTRACT

The contamination profile and the human health risk assessment of various heavy metals (Cd, Cr, Mn, Ni and Pb) in vegetable oils, palm oils, butter and shea butter purchased from the Nigerian market were evaluated. Univariate and multivariate analyses including the principal component analysis (PCA), hierarchical cluster analysis (HCA) and heat map visualization were used to evaluate correlation, similarity and source of metals. Dietary intake and dermal absorption through the application in skin were also assessed. The heavy metals 5th and 95th percentile interval range (in mg/kg) were 0.003–0.208, 0.003–0.392, 0.003–1.344, 0.003–0.369 and 0.006–0.531 for Cd, Cr, Mn, Ni and Pb, respectively. Concentrations of Cr and Mn were significantly different across sample categories, being the levels of Mn and Ni positively correlated in both oil and butter samples. The result of PCA, HCA and heat map revealed the profile of heavy metals in oils was different from that of butters, with Pb mainly associated to oils, and Cd, Cr, Mn and Ni to butters. In some samples, the international maximum levels for Cd, Ni and Pb in edible oils were exceeded. Cadmium and Pb dietary intake through Nigerian oils and butters should not be considered negligible for human health protection.

1. Introduction

Vegetable oils constitute the main cooking oils consumed by humans. They possess a rich content of essential fatty acids, phytosterols, tocopherol, as well as high levels of antioxidative nutrients like monosaturated fatty acids, which unlike animal fats, are predominantly saturated (Dugo et al., 2004). Dietary oils and butter are utilised by the human body for various vital activities such as energy source, structural component, and to make powerful biological regulators (Mendil et al., 2009). In addition, some oils and butter (i.e., shea butter) have been commonly applied to the skin since their anti-inflammatory, antioxidant, wound healing, anti-bacterial, and skin barrier restoration properties (Lin et al., 2018).

Metals and metalloids in edible fats (oils and butters) tend to heighten oxidative process and eventual generation of free radicals from fatty acids or hydroperoxides (Galeano Díaz et al., 2006; Jiang et al., 2020). Therefore, it is necessary to understand the relevance of the metal content in edible fats, but also the potentially associated human health risks of metals and metalloids in these foods. The diet is the main exposure pathway for both organic and inorganic contaminants like metals and metalloids. Taking this into account, a number of researchers have appraised the concentrations of metals and metalloids in edible fats such vegetable oils and butters (Pehlivan et al., 2008; Zhu et al., 2011; Mendil et al., 2009; Cindric et al., 2007; Perelló et al., 2015; González et al., 2021).

In view of the metabolic role of some metals -especially transition metals-it is important for public health to evaluate the risk assessment of metals in commercially available edible fats, specifically in the Niger Delta Region, Nigeria (APHA (American Herbal Products Association), 2009; Colak et al., 2005). The metal content in cooking and edible oils and butters is considered crucial from toxicological standpoints. Metals present in edible fats may be of natural origin or incorporated during

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Table 1
Levels of various metals (mg/kg) in oils and butter from the Nigerian market.

		Cd	Cr	Mn	Ni	Pb
Vegetable oils (n = 13)	Mean	0.025	0.007	0.084	0.183	0.248
	SD	0.019	0.008	0.113	0.159	0.208
	Median	0.025	0.003	0.024	0.132	0.217
	P5	0.004	0.003	0.003	0.017	0.007
	P95	0.055	0.022	0.269	0.414	0.587
Palm oils (n = 6)	Mean	0.037	0.017	0.017	0.148	0.105
	SD	0.016	0.023	0.018	0.140	0.125
	Median	0.032	0.008	0.012	0.127	0.060
	P5	0.020	0.003	0.003	0.020	0.009
	P95	0.059	0.051	0.041	0.331	0.289
Local shea butter (n = 5)	Mean	0.054	0.234	0.945	0.216	0.212
	SD	0.069	0.291	0.944	0.162	0.237
	Median	0.007	0.141	0.596	0.215	0.190
	P5	0.003	0.007	0.169	0.035	0.006
	P95	0.137	0.628	2.175	0.411	0.521
Refined shea butter (n = 7)	Mean	0.067	0.136	0.370	0.060	0.133
	SD	0.070	0.119	0.493	0.060	0.117
	Median	0.059	0.117	0.260	0.034	0.137
	P5	0.006	0.031	0.044	0.006	0.021
	P95	0.175	0.319	1.119	0.151	0.303
Local butter (n = 6)	Mean	0.074	0.121	0.242	0.079	0.138
	SD	0.109	0.157	0.111	0.087	0.113
	Median	0.022	0.054	0.280	0.056	0.135
	P5	0.003	0.003	0.079	0.003	0.018
	P95	0.239	0.352	0.329	0.197	0.288
Refined butter (n = 6)	Mean	0.115	0.198	0.188	0.144	0.118
	SD	0.113	0.275	0.160	0.143	0.103
	Median	0.100	0.081	0.195	0.132	0.112
	P5	0.011	0.003	0.010	0.006	0.016
	P95	0.247	0.606	0.394	0.300	0.225

SD: standard deviation; P5 and P95: percentile 5th and 95th, respectively.

processing procedures (Nunes et al., 2011). Although the occurrence of these metals (and metalloids) in edible vegetable fats may be derived from source of plantation and manufacture, environmental exposure can also influence negatively the quality of the edible vegetable oils and butter by elevating the levels of toxic metals and metalloids (Bakircioglu et al., 2013).

Furthermore, the concentrations of metals in cooking and edible fats are an important criterion for the assessment of quality with regard to freshness, keeping properties, storage, and their influence on human nutrition and health (Lepri et al., 2011). The deleterious effects of metals on the flavour and oxidative stability of oils should be also considered taking into account that some elements could catalyse oxidation of fatty acid chains, exerting a deleterious influence on shelf life and nutritional value (Galeano Díaz et al., 2006). The metal profile is subject to food legislation (Cypriano et al., 2008), and it is used for detecting adulterations in oils (Gonzálvez et al., 2010).

Metals such as cadmium (Cd), chromium (Cr), manganese (Mn), nickel (Ni) and lead (Pb) may negatively affect people's health. Cadmium is known to accumulate in human body and may induce kidney dysfunction, skeletal damage, and adverse reproductive effects (Forte and Bocca, 2011; Oggiano et al., 2021). In turn, Cr is an essential nutrient for humans as it is involved in the glucose tolerance. Adequate Cr nutrition may reduce risk factors associated with cardiovascular disease, as well as diabetes mellitus. However, hexavalent Cr is potentially toxic and carcinogenic (Reilly, 2002). On the other hand, various studies identified that the deficiency of Mn can result in severe skeletal and reproductive abnormalities in mammals, while high doses of Mn produce adverse effects primarily on the lungs and on the brain (International Programme on Chemical Safety (IPCS), 1999). With respect to Ni, trace amounts of this metal may be beneficial as an activator of some enzyme systems, but its toxicity at high levels can be prominent. This metal may provoke allergies in particularly sensitive consumers: people suffering from a contact allergy to Ni may have been previously sensitized by the amounts of Ni present in food or drink (Cristaudo et al., 2019; Petrucci et al., 2009). Finally, Pb is a cumulative element that affects multiple body systems, including the neurological, haematological, gastrointestinal, cardiovascular and renal systems (Forte and Bocca, 2011; Farace et al., 2020). In addition, Pb accumulates and substitute's Ca in bone tissues and the resultant effect is disruption of mineralization, alteration of compositional properties, and bone formation mechanisms (Gangoso et al., 2009).

The present study was aimed at determining: i) the concentrations of Cd, Cr, Mn, Ni and Pb in vegetable oils, palm oil, butter and shea butter purchased from the Nigerian market; ii) the correlation, similarity and source of these metals in samples using both univariate and multivariate statistical analyses including the principal component analysis (PCA), hierarchical cluster analysis (HCA) and heat map visualization, and iii) the estimated daily intake of these metals through the diet and dermal absorption of oils and butters.

2. Materials and methods

2.1. Study area and sample collection

The Niger Delta Region falls within the central coastlands of southern Nigeria. It is situated in the Gulf of Guinea at the intersection of latitude 5°31 N and 5°33 N, and longitude 5°30 E and 5°32 E. It is the largest wetland in Africa and the third largest in the world, consisting of flat low lying swampy terrain, which is criss-crossed by meandering streams, rivers and creeks (Ana et al., 2011).

A total of 43 samples, classified as vegetable oils (n = 13), palm oils (n = 6), local butter (n = 6), refined butter (n = 6), local shea butter (n = 5) and refined shea butter (n = 7), were purchased from local markets in Port Harcourt, Abua, Elele, Ubima and Etche areas, all in Rivers State, Niger Delta, Nigeria, in March 2019. All samples were measured as wet weight. Immediately after acquisition, samples were packaged in glass petri dishes, and kept in the laboratory until analyses of metals.

2.2. Analysis of metals

The concentrations of Cd, Cr, Mn, Ni and Pb in 43 oil and butter samples were determined. The analytical procedure was previously reported (Okoye et al., 2021a). Briefly, 5 g of each sample were digested in 9 mL of 65% HNO_3 (Merck, Darmstadt, Germany) and 3 mL of perchloric acid (Merck, Darmstadt, Germany) in a hot plate at 110 °C for 5 h. Afterwards, samples were introduced into an oven under a temperature that was gradually increased in 100 °C every 60 min, until the requested final temperature of 450 °C was reached. Finally, 18 h later, white ashes were obtained. After cooling, white ashes were dissolved in 5 mL of HNO_3 (1.5%) and make up to 25 mL with deionized water. The resulting solution was filtered using a Whatman filter paper (number 42) fitted into a Buchner funnel, before being transferred into a tightly sealed plastic container. A GBC Sense AA 800G high-resolution continuum source atomic absorption spectrometer (SE-710690), coupled to graphite furnace (Cambridge CB5 8BZ, *Cambridgeshire*, UK), was used for metal analysis.

2.3. Quality control

All chemical reagents and solvents used were of picograde quality. To achieve reproducible and reliable results, in the analyses of Cd, Cr, Mn, Ni and Pb, the instrument was recalibrated after every ten runs. The analytical procedure was checked using spike recovery method (SRM). For it, a known standard of elements was spiked into already analyzed samples and reanalyzed. High purity multi-cathode lamp (1000 mg/kg) from Cambridge CB5 8BZ (*Cambridgeshire*, UK) was used to obtain the calibration curves for each metal. The multi-element calibration curves were verified with a multi-element certified material of 1000 mg/kg (Cambridge CB5 8BZ, *Cambridgeshire*, UK). The percentages of recovery varied between 94.5 and 100%. The relative standard deviation between replicate analyses was less than 4%. The limits of detection (LoD),

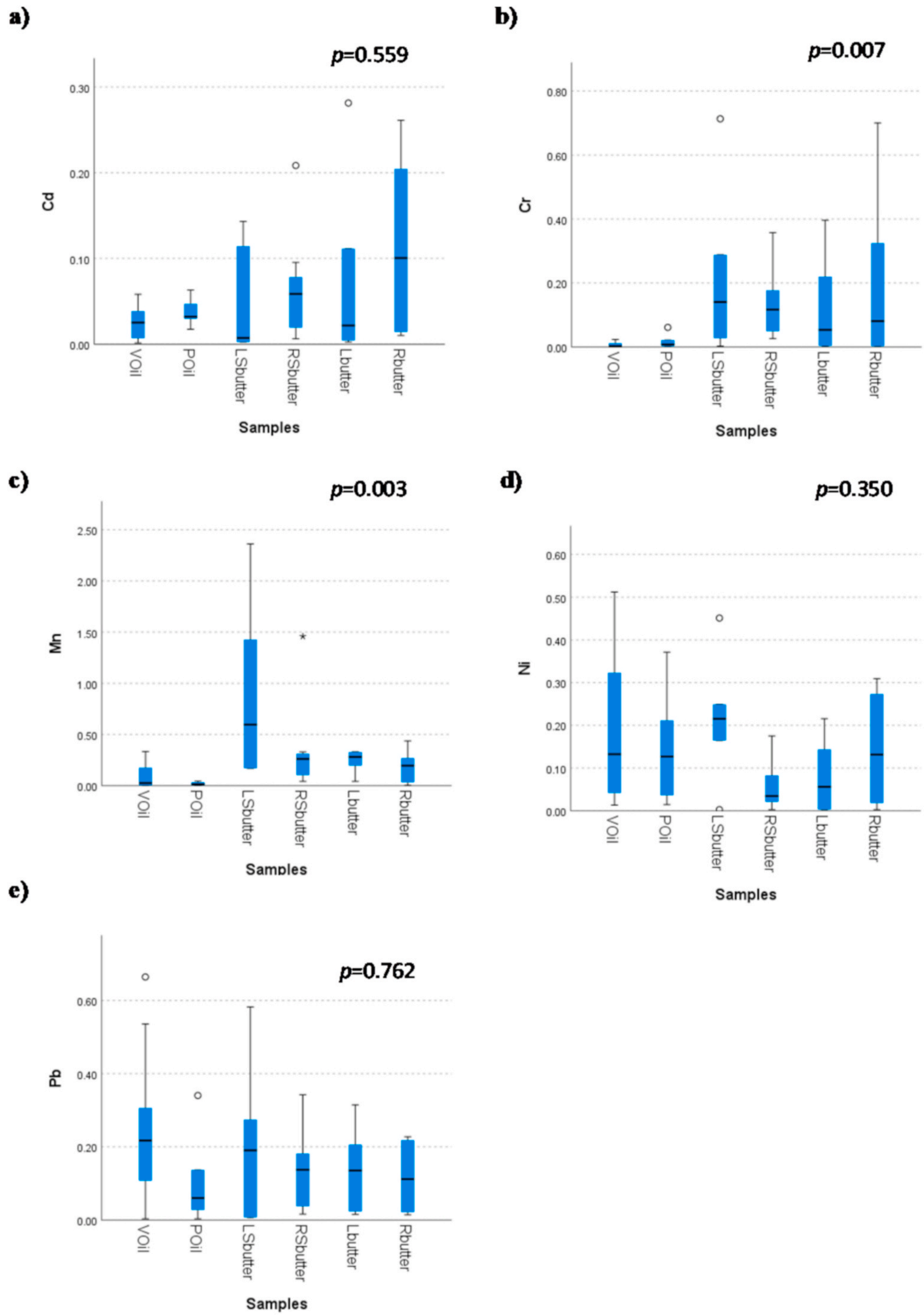

Fig. 1. Metals (a: Cd; b: Cr; c: Mn; d: Ni; e: Pb) levels in samples of oils and butters from the Nigerian market (VOil: vegetable oils; POil: palm oil; LSbutter: local shea butter; RSbutter: refined shea butter; L: local butter; Rbutter: refined butter).

calculated as 3-times the standard deviation (SD) from 10 replicated measurements of a representative sample, were the following: 0.001 mg/kg for Cd, Cr, Mn and Ni, and 0.01 mg/kg for Pb. The limits of quantification (LoQ), calculated as 10 times the SD, were the following: 0.0033 mg/kg for Cd, Cr, Mn and Ni, and 0.033 mg/kg for Pb.

2.4. Univariate and multivariate statistical analyses

The Kruskal-Wallis test was used to detect statistically significant differences between samples using p values, effect size (η^2), and pairwise comparisons adjusted by the Bonferroni correction (Wasserstein and Lazar, 2016). In addition, the Spearman' correlation analysis was employed to ascertain the interrelationships between the analyzed metals and the Spearman's correlation coefficients (rho values), being ssociated 95% confidence intervals (CIs) and p-values calculated.

A combination of Principal Component Analysis (PCA), hierarchical cluster analysis (HCA), and heat map were used for the multivariate analysis, and applied to the complete data set. In the PCA, the Varimax rotation extraction method with Kaiser normalization was used. Eigenvalues >1 were adopted as the significant benchmark for the principal components (PCs). Three PCs (PC1, PC2 and PC3) were above 1 in the data set, and hence, were extracted for further analysis. Afterwards, the

Table 2
Spearman's correlation coefficients (rho values) and 95th confidence interval (CIs) of metals in Nigerian oils and butters.

Samples		Cd	Cr	Mn	Ni	Pb
Oils	Cd	1				
	Cr	−0.020 [-0.4699, 0.4382]	1			
	Mn	−0.556* [-0.8065, -0.1362]	0.252 [-0.2283, 0.6337]	1		
	Ni	0.032 [-0.4284, 0.4792]	0.176 [-0.3024, 0.5836]	0.462* [0.0099, 0.7573]	1	
	Pb	0.236 [-0.2444, 0.6234]	−0.158 [-0.5712, 0.3191]	−0.392 [-0.7183, 0.0757]	−0.402 [-0.7240, 0.0639]	1
Butter	Cd	1				
	Cr	−0.151 [-0.5226, 0.2688]	1			
	Mn	0.177 [-0.2438, 0.5417]	−0.079 [-0.4675, 0.3351]	1		
	Ni	0.400 [-0.0041, 0.6918]	0.057 [-0.3545, 0.4500]	0.525** [0.1543, 0.7661]	1	
	Pb	0.046 [-0.3642, 0.4412]	−0.015 [-0.4159, 0.3908]	0.135 [-0.2839, 0.5106]	0.353 [-0.0588, 0.6621]	1
Oils and Butter	Cd	1				
	Cr	−0.023 [-0.3211, 0.2793]	1			
	Mn	0.057 [-0.2476, 0.3513]	0.291 [-0.0102, 0.5438]	1		
	Ni	0.278 [-0.0244, 0.5338]	−0.155 [-0.4351, 0.1524]	0.244 [-0.0608, 0.5072]	1	
	Pb	0.135 [-0.1723, 0.4184]	−0.135 [-0.4184, 0.1723]	−0.137 [-0.4201, 0.1704]	0.034 [-0.2691, 0.3310]	1

Oils include vegetable oils and palm oil categories. Butter includes local and refined shea butter, and refined and local butter.
*$p < 0.05$; **$p < 0.01$.

Table 3
Eigenvalues and variance of Principal Component Analysis (PCA) of metals in oils and butter samples.

	Oils and Butter		
	PC1	PC2	PC3
Cd	0.735	−0.180	0.124
Cr	0.044	−0.041	0.976
Mn	0.580	0.481	0.226
Ni	0.765	0.158	−0.105
Pb	−0.017	0.914	−0.088
Eigenvalue (total)	1.464	1.126	1.039
Variability (%)	29.28	22.51	20.77
Cumulative %	29.28	51.80	72.57

PCA with Varimax rotation method.
Values in bold have moderate to strong factor loadings.

PCs were represented by a coordinate axis projected in a three-dimensional graph (for the three PCs) for an easier spatial visualization of the data. In the HCA, the clusters were determined by the Ward's method and squared Euclidean measure, being shown in dendrograms. In addition, the two-dimensional heat map was composed with the colour map according to the correlation of each metal with samples. Statistical analysis was performed with the SPSS software, version 2020 (SPSS Inc., Chicago, IL, USA).

2.5. Estimated daily intake and risk assessment

Metal intakes through oil and butter consumption were calculated using equation (1), while dermal absorption due to application of oils and butters were calculated using equation (2). Dermal and dietary intake assessments were done probabilistically using Montecarlo simulation with the Oracle Crystal ball software (version 11.1.2.4.850). Propagation of variability and uncertainty were conducted using a probability function for each parameter and until reaching 100,000 iterations. Probabilistic approach in exposure and risk assessment is commonly used in exposure and risk assessment in order to solve data scarcity and uncertainty (Batista et al., 1996; Okoye et al., 2021a,b; Rovira et al., 2016).

$$\text{Dietary intake} = IR \times C/BW \quad (1)$$

$$\text{Dermal absorption} = Ap \times C \times ABS/BW \quad (2)$$

where Dietary intake is the intake of metals through consumption of oils and butter in μg/kg/day; IR is the ingestion rate of vegetable oil and butter (in g/day); C is the concentration of metals in vegetable oils and fat (in μg/g) obtained in present study; BW is the body weight (70 ± 10.3 kg) (Ihedioha et al., 2014). In turn, Dermal absorption is the absorption through the skin due to the application of oils and fats in the whole body and the lips (in μg/kg/day); Ap is the amount of oil or butter applied to the skin (8.69 ± 5.09 g and 0.024 ± 0.034 g for whole body and lips, respectively) (Loretz et al., 2005); ABS (unitless) is the absorption rate for each metal (0.01, 0.002, 0.03, 0.008 and 0.003 for Mn, Ni, Cr, Cd, and Pb, respectively (Lim et al., 2018)). Since the data scarcity, IR of vegetable oils and butter was assumed to be 29.4 ± 4.3 g/day, which is the mean (±standard deviation) obtained from studies conducted in Kenya, Nigeria and Spain (Iwegbue et al., 2021; Partearroyo et al., 2019; Steyn and Nel, 2016), as well as data from food supply from the Food and Agriculture Organization (FAO) (FAOSTAT, 2021). For C, BW and Ap parameters, a logarithmic normal distribution was used. However, due to the lack of data, for IR and ABS a normal distribution was used.

3. Results and discussion

The levels of Cd, Cr, Mn, Ni and Pb in Nigerian oils and butters are shown in Table 1. The mean Cd concentration in samples ranged between 0.025 ± 0.019 mg/kg in vegetable oils and 0.115 ± 0.113 mg/kg in refined butter. The Kruskal-Wallis test did not show no differences between the mean ranks of all groups ($p = 0.559$) with the observed effect size, which was small (η^2 -0.028). There were no significant differences also comparing any pair of groups (Fig. 1a). For Cad, the Codex Alimentarius for contaminants and toxins in food and feed has

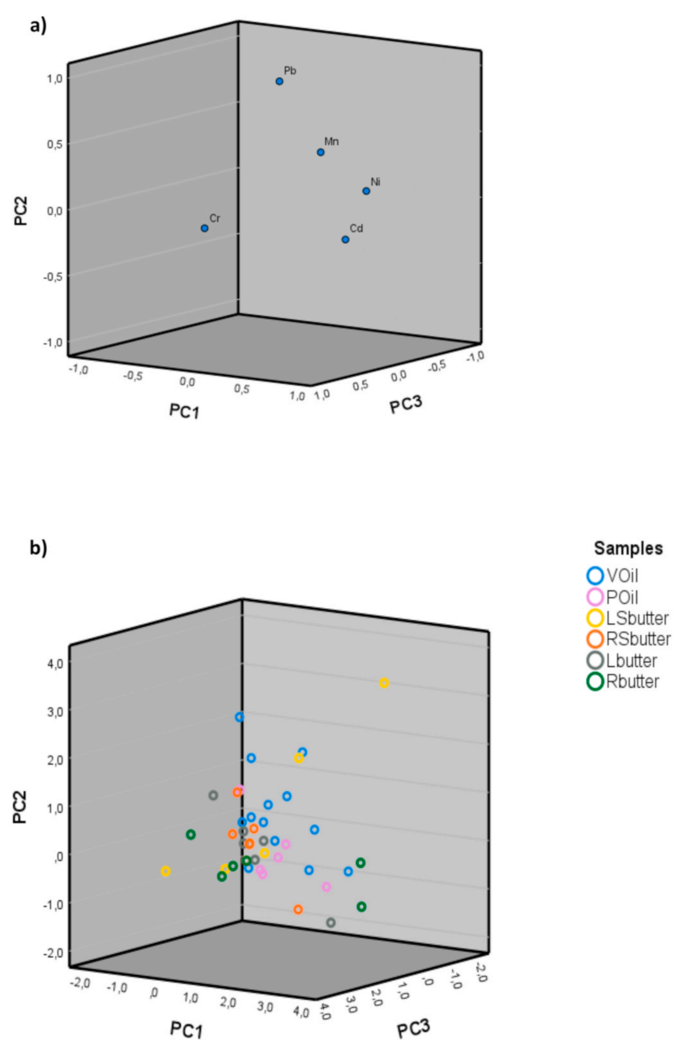

Fig. 2. Principal Component analysis (PCA) with Varimax rotation method of metals in sample of oils and butter: a) component plot by variables (metals); b) component plot by samples (VOil: vegetable oils; POil: palm oil; LSbutter: local shea butter; RSbutter: refined shea butter; L: local butter; Rbutter: refined butter).

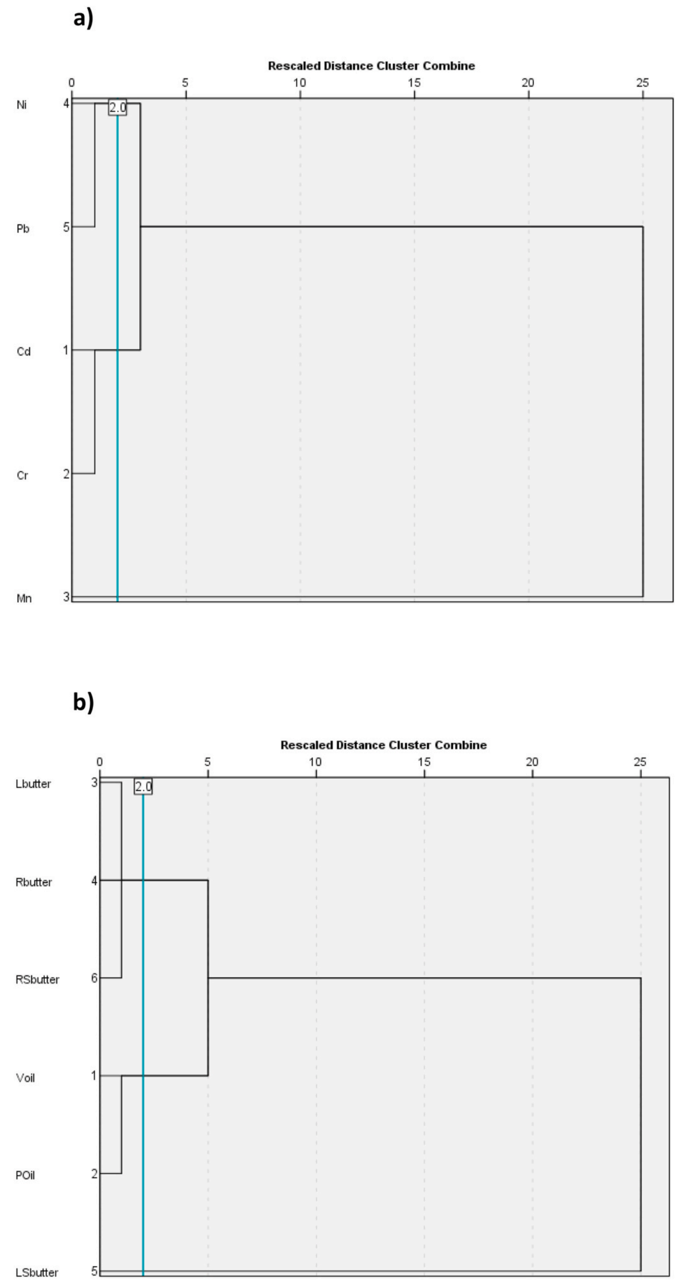

Fig. 3. Hierarchical cluster analysis (HCA) using Ward's method and squared Euclidean measure of metals in oils and butter: a) cluster by variables (metals); a) cluster by samples (VOil: vegetable oils; POil: palm oil; LSbutter: local shea butter; RSbutter: refined shea butter; L: Local butter; Rbutter: refined butter).

established a maximum level (ML) of 0.1 mg/kg in edible vegetable oils (FAO, 2001). In the current survey, 19% (8 out 43) of the analyzed samples exceeded this limit. A previous study carried out in Abia State, South-eastern Nigeria (Nnorom et al., 2014), reported levels of Cd in palm oil of 0.064 ± 0.020 mg/kg, which are comparable to the levels of palm oil found in the present study (0.037 ± 0.016 mg/kg). In vegetable oils sold in Zaria (Northern Nigeria), the lowest and highest Cd values were 0.34 and 2.77 mg/kg, respectively (Ogabiela et al., 2010). In turn, in samples of edible vegetable oils produced in Iran, Cd was found to be 1.87–8.58 μg/kg (Farzin and Moassesi, 2014).

The levels of Cr were significantly different ($p = 0.007$) among oil and butter samples (Fig. 1b), showing the lowest mean concentration in vegetable (0.007 ± 0.008 mg/kg) and palm (0.017 ± 0.023 mg/kg) oils, and the highest in butter samples, with the maximum value detected in local shea butter (0.234 ± 0.291 mg/kg). The Kruskal-Wallis test showed a difference between the mean ranks of all groups ($p = 0.007$) with the observed effect size equal to η^2 -0.23, indicating that the magnitude of the difference between averages was large. In addition, there were significant differences comparing vegetable oils and refined shea butter ($p = 0.015$ adjusted by the Bonferroni correction) (Fig. 1a). There are currently no maximum levels in the EU legislation for total Cr in foodstuffs. Around the world, China released the National Food Safety Standard of Maximum Levels of Contaminants in Foods, which sets the limit for Cr in milk and milk products at 0.3 mg/kg (Clever and Jie, 2014). In previous investigations also conducted in Nigeria, the overall mean concentration of Cr in palm oil samples from Abia State was 0.176 ± 0.048 mg/kg (range 0.101–0.298 mg/kg) (Nnorom et al., 2014), which was higher than the levels found in Lagos (0.021–0.033 mg/kg) (Adepoju-Bello et al., 2012).

Manganese presented lower levels in vegetable (0.084 ± 0.013 mg/kg) and palm (0.017 ± 0.018 mg/kg) oils than in butter, especially for local shea butter (0.945 ± 0.944 mg/kg) and refined shea butter (0.370 ± 0.493 mg/kg). As for Cr levels, Mn concentration was significantly ($p = 0.003$) different across all sample categories (Fig. 1c) with large effect size (η^2 0.36). In particular, values for palm oils and local shea butter were significantly different ($p = 0.019$) according to the Bonferroni

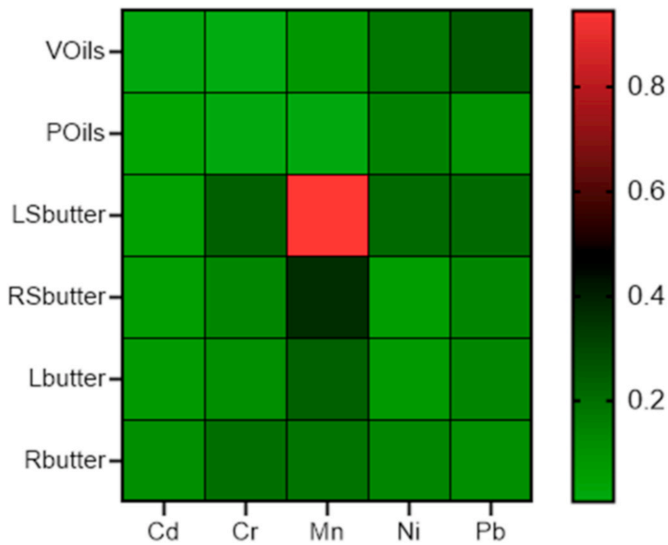

Fig. 4. Heat map of correlation for metals in oils and butter (VOil: vegetable oils; POil: palm oil; LSbutter: local shea butter; RSbutter: refined shea butter; L: local butter; Rbutter: refined butter). Red: strong positive correlation; green: week correlation. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

criterion. There are currently no maximum authorized levels for Mn in foodstuffs. In the current survey, Mn levels were lower than those previously reported in Nigerian palm oils (6.55–12.05 mg/kg) (Nnorom et al., 2014). However, they were more comparable with data from different varieties of vegetable oils purchased in China (from 0.113 mg/kg in olive oil to 0.556 mg/kg in peanut oil) (Zhu et al., 2011).

Regarding Ni, this metal presented the lowest concentration in refined shea butter (0.060 ± 0.060 mg/kg) and the highest one in vegetable oil (0.183 ± 0.159) and in local shea butter (0.216 ± 0.162 mg/kg), with no significant differences ($p = 0.350$ and effect size of η^2 0.015) among all sample kinds (Fig. 1d). According to international requirements, the content of Ni in oils should not surpass 0.2 mg/kg, while the 35% (15 out 43) of the analyzed samples exceeded this value (Kowalewska et al., 2005). The Ni levels observed in the current study were higher than those reported in the scientific literature for Spanish (Llorent-Martínez et al., 2011) and Turkish edible oils (Pehlivan et al., 2008), but lower than those found in Nigerian oils (Nnorom et al., 2014; Adepoju-Bello et al., 2012; Ogabiela et al., 2010). In samples from China, the Ni content ranged between 0.026 mg/kg in peanut oil and 0.075 mg/kg in sesame oil (Zhu et al., 2011).

In relation to Pb, the highest concentration was detected in vegetable oils (0.248 ± 0.208) and the lowest in refined butter (0.118 ± 0.103). The refining process may be efficient on metal removal. Results from an ITERG study (1992–1999) noticed that all the analyzed refined samples did not present any Pb, while 20% of the analyzed cold pressed oils might contain Pb between 0.02 and 0.1 mg/kg (Lacoste, 2014). No significant ($p = 0.762$) differences were observed in Pb levels between sample categories (Fig. 1e) with a small observed effect size (η^2 -0.066).

The levels of Pb here detected were higher than those found in palm oils purchased from Lagos (0.022–0.038 mg/kg) and Abia State (0.024–0.067 mg/kg) (Adepoju-Bello et al., 2012; Nnorom et al., 2014). Notwithstanding, they were comparable to the levels reported in vegetable oils (0.01–0.34 mg/kg) purchased from Zaria (Nigeria) (Ogabiela et al., 2010). Lower levels of Pb were detected in edible vegetable oils from Italy and Turkey, where concentrations ranged between 0.005 and 0.043 mg/kg and 0.04–0.11 mg/kg, respectively (Dugo et al., 2004). Concentrations of Pb in edible vegetable oils were reported to be 0.028–0.064 mg/kg in China and 4.56–15.82 μg/kg in Iran (Zhu et al., 2011; Farzin and Moassesi, 2014). The Codex Alimentarius and the European legislation established a maximum of 0.10 mg/kg for Pb in oil and butters (FAO, 2001; EU Commission Regulation (EC), 2001). In the present study, around the 60% (23 out 43) of samples exceed that limit for Pb. The results of the Spearman's correlation analysis (Table 2) showed the negative correlation between Cd and Mn (rho value and 95% CI: 0.556 [−0.8065, −0.1362]; $p < 0.05$), as well as the positive correlation between Mn and Ni (rho value and 95% CI: 0.462 [0.0099, 0.7573]; $p < 0.05$) in oils (including vegetable and palm oils). In butter samples (including also shea butter), the only significant positive correlation was between Mn and Ni (rho value and 95% CI: 0.525 [0.1543, 0.7661]; $p < 0.01$), as also observed in oils. The 95% CIs did not include the zero value thus providing precision of the observed correlations without uncertainty or ambiguity left by the data. Considering the whole data set (oil plus butter samples), no significant ($p > 0.05$) correlations between metals were found.

The eigenvalues and variance of PCA applied to all samples of oils and butter are reported in Table 3. Based on PCA, the first three PCs explained 72.6% of the total variance, suggesting a good quality of the three-dimensional graphical representations of the dataset. Moreover, the Varimax orthogonal rotation (that assumed independent or uncorrelated factors) with Kaiser normalization (to obtain stability of solutions across samples) permitted to minimize the loss of variance due to not using all the PCs, which made interpretation of dimensions easier. The PC1 explained up to 29.3% of the total variance, being characterized by high positive loadings of Cd (0.735), Mn (0.580) and Ni (0.765). The PC2 explained 22.5% of the total variance, being dominated only by Pb (0.914). Finally, the PC3 explained 20.8% of the total variance and was dominated by Cr (0.976). Fig. 2 shows the three principal component plot, indicating that Cd, Mn and Ni were the most correlated metals. In turn, Cr and Pb formed a big angle with the other metals, confirming that there are no correlation between these metals and the remaining elements (Fig. 2a) as previously found with Spearman's correlation analysis (Table 2). The PC1 component was better represented by butter than by oil samples, and across this component, the higher loadings were associated to Cd, Mn and Ni (Fig. 2a and b). In particular, Cd appeared mainly associated to refined butter samples, presenting high concentration values (0.20–0.28 mg/kg) in three samples of margarine. Manganese was associated with various types of butter, with the highest values found in local and refined shea butter samples (interval 1.4–2.4 mg/kg). Some local shea butter samples, which showed higher Mn levels, presented also high Ni levels (0.25–0.50 mg/kg). On the other hand, PC2 seemed to separate vegetable oil samples from the rest of the samples, being this PC component very influenced by the content of Pb (Fig. 2a and b). Some vegetable oils and one palm oil sample presented the highest Pb concentration in comparison to the others samples, which varied from 0.31 mg/kg in soya oil to 0.54 mg/kg in extra virgin olive oil. A slight separation between butter samples from oil samples was also observed across the PC3 component, which is mainly represented by Cr (Fig. 2a and b). Butter samples presented more than 10-fold higher Cr concentration respect to that in oil samples as shown in Table 1.

HCA can be used as an alternative method to confirm PCA results and provide grouping of variables and samples. The HCA results for the heavy metals in samples are depicted in Fig. 3. The dendrogram of Fig. 3a shows that Ni and Pb formed one cluster with distance lower than 2 units, as well as Cr and Cd that were clustered together. In contrast, Mn was distant by 25 units from the other elements. Therefore, metals as Cd, Cr, Ni and Pb may come from similar sources, while Mn could have a different origin. In general, the contamination of oils and butters with metals may be due to soil contamination, application of fertilisers and/or metal containing pesticides, and production process or metal processing equipment (Lacoste, 2014). In particular, the presence of some metals as Cd, Cr and Pb in samples might be associated to anthropogenic activities as fertilizer and vehicle emission, while Mn and Ni levels may be controlled by original materials and, therefore, considered as natural sources. The dendrogram in Fig. 3b showed two distinct clusters, namely one cluster constituted by local butter, refined butter and refined shea

Table 4
Dietary intake and dermal absorption (μg/kg/day) of metals in oils and butters from the Nigerian market.

		Dietary intake					Dermal absorption				
		Cd	Cr	Mn	Ni	Pb	Cd	Cr	Mn	Ni	Pb
Vegetable oils	Mean	1.1E-02	3.1E-03	3.6E-02	7.9E-02	1.1E-01	2.6E-05	2.8E-05	1.1E-04	4.8E-05	9.5E-05
	SD	8.8E-03	3.4E-03	5.1E-02	7.2E-02	9.4E-02	2.7E-05	3.7E-05	1.8E-04	6.6E-05	1.2E-04
	P50	8.5E-03	2.1E-03	2.1E-02	5.8E-02	8.0E-02	1.8E-05	1.6E-05	5.4E-05	2.8E-05	5.9E-05
	P75	1.4E-02	3.8E-03	4.3E-02	9.8E-02	1.3E-01	3.2E-05	3.3E-05	1.2E-04	5.8E-05	1.2E-04
	P95	2.7E-02	9.1E-03	1.2E-01	2.1E-01	2.8E-01	7.5E-05	8.9E-05	3.7E-04	1.6E-04	3.0E-04
Palm oil	Mean	1.6E-02	7.4E-03	7.5E-03	6.4E-02	4.6E-02	3.7E-05	6.6E-05	2.2E-05	3.9E-05	4.0E-05
	SD	7.8E-03	1.0E-02	7.9E-03	6.3E-02	5.8E-02	2.9E-05	1.1E-04	3.0E-05	5.6E-05	6.4E-05
	P50	1.4E-02	4.3E-03	5.2E-03	4.5E-02	2.9E-02	3.0E-05	3.3E-05	1.3E-05	2.2E-05	2.0E-05
	P75	2.0E-02	8.7E-03	9.3E-03	7.9E-02	5.5E-02	4.8E-05	7.4E-05	2.7E-05	4.6E-05	4.5E-05
	P95	3.1E-02	2.3E-02	2.2E-02	1.8E-01	1.4E-01	9.3E-05	2.3E-04	7.1E-05	1.3E-04	1.4E-04
Local Shea butter	Mean	2.3E-02	1.0E-01	4.1E-01	9.4E-02	9.2E-02	5.5E-05	8.9E-04	1.2E-03	5.7E-05	8.1E-05
	SD	3.0E-02	1.2E-01	4.3E-01	7.4E-02	1.1E-01	9.0E-05	1.4E-03	1.6E-03	7.1E-05	1.2E-04
	P50	7.1E-03	3.2E-02	1.6E-01	4.6E-02	3.2E-02	2.9E-05	4.8E-04	7.2E-04	3.5E-05	4.3E-05
	P75	2.8E-02	1.2E-01	5.0E-01	1.2E-01	1.1E-01	6.2E-05	1.0E-03	1.4E-03	7.0E-05	9.3E-05
	P95	7.3E-02	3.1E-01	1.2 E+00	2.3E-01	2.7E-01	1.9E-04	3.1E-03	3.9E-03	1.8E-04	2.8E-04
Refined Shea butter	Mean	2.9E-02	5.9E-02	1.6E-01	2.6E-02	5.8E-02	6.8E-05	5.2E-04	4.7E-04	1.6E-05	5.1E-05
	SD	3.2E-02	5.5E-02	2.2E-01	2.7E-02	5.3E-02	9.6E-05	6.1E-04	7.8E-04	2.4E-05	6.5E-05
	P50	1.9E-02	4.4E-02	9.4E-02	1.8E-02	4.3E-02	4.0E-05	3.3E-04	2.4E-04	8.4E-06	3.1E-05
	P75	3.5E-02	7.4E-02	1.9E-01	3.2E-02	7.2E-02	8.1E-05	6.4E-04	5.3E-04	1.8E-05	6.2E-05
	P95	8.4E-02	1.6E-01	5.1E-01	7.3E-02	1.5E-01	2.2E-04	1.6E-03	1.7E-03	5.3E-05	1.6E-04
Local butter	Mean	3.2E-02	5.3E-02	1.0E-01	3.4E-02	6.0E-02	7.5E-05	4.6E-04	3.1E-04	2.1E-05	5.3E-05
	SD	4.8E-02	7.1E-02	5.3E-02	3.9E-02	5.1E-02	1.4E-04	7.4E-04	2.5E-04	3.3E-05	6.5E-05
	P50	1.7E-02	3.2E-02	9.3E-02	2.3E-02	4.5E-02	3.6E-05	2.4E-04	2.4E-04	1.1E-05	3.3E-05
	P75	3.7E-02	6.3E-02	1.3E-01	4.2E-02	7.5E-02	8.2E-05	5.3E-04	4.0E-04	2.4E-05	6.5E-05
	P95	1.1E-01	1.7E-01	2.1E-01	1.0E-01	1.5E-01	2.7E-04	1.6E-03	7.8E-04	7.2E-05	1.7E-04
Refined butter	Mean	5.0E-02	8.6E-02	8.2E-02	6.2E-02	5.1E-02	1.2E-04	7.6E-04	2.4E-04	3.8E-05	4.5E-05
	SD	5.0E-02	1.3E-01	7.3E-02	6.5E-02	4.6E-02	1.5E-04	1.3E-03	2.8E-04	5.6E-05	5.8E-05
	P50	3.5E-02	4.9E-02	6.1E-02	4.3E-02	3.7E-02	7.1E-05	3.8E-04	1.6E-04	2.0E-05	2.7E-05
	P75	6.2E-02	1.0E-01	1.0E-01	7.7E-02	6.3E-02	1.4E-04	8.5E-04	3.0E-04	4.4E-05	5.5E-05
	P95	1.4E-01	2.8E-01	2.1E-01	1.8E-01	1.3E-01	3.7E-04	2.7E-03	7.3E-04	1.3E-04	1.4E-04
Oils	Mean	1.3E-02	4.5E-03	2.7E-02	7.4E-02	8.8E-02	3.0E-05	4.0E-05	8.0E-05	4.5E-05	7.7E-05
	SD	8.5E-03	6.5E-03	4.3E-02	6.8E-02	8.9E-02	2.9E-05	6.8E-05	1.6E-04	6.1E-05	1.0E-04
	P50	1.0E-02	2.6E-03	1.4E-02	5.5E-02	6.2E-02	2.1E-05	2.0E-05	3.6E-05	2.6E-05	4.5E-05
	P75	1.6E-02	5.2E-03	3.1E-02	9.3E-02	1.1E-01	3.7E-05	4.4E-05	8.6E-05	5.4E-05	9.3E-05
	P95	2.9E-02	1.5E-02	9.1E-02	2.0E-01	2.5E-01	8.2E-05	1.4E-04	2.9E-04	1.5E-04	2.5E-04
Butter	Mean	3.4E-02	7.3E-02	1.8E-01	5.1E-02	6.3E-02	8.0E-05	6.4E-04	5.2E-04	3.1E-05	5.6E-05
	SD	4.1E-02	9.2E-02	2.5E-01	5.6E-02	6.3E-02	1.2E-04	9.8E-04	8.5E-04	4.8E-05	7.7E-05
	P50	2.2E-02	4.5E-02	1.0E-01	3.4E-02	4.5E-02	4.4E-05	3.5E-04	2.7E-04	1.6E-05	3.3E-05
	P75	4.1E-02	8.8E-02	2.1E-01	6.3E-02	7.8E-02	9.3E-05	7.4E-04	5.8E-04	3.6E-05	6.8E-05
	P95	1.0E-01	2.2E-01	5.7E-01	1.5E-01	1.8E-01	2.7E-04	2.2E-03	1.8E-03	1.1E-04	1.8E-04
Oils + butter	Mean	2.4E-02	4.3E-02	1.1E-01	6.1E-02	7.4E-02	5.8E-05	3.7E-04	3.3E-04	3.7E-05	6.6E-05
	SD	3.2E-02	7.8E-02	2.0E-01	6.2E-02	7.5E-02	9.3E-05	7.9E-04	7.2E-04	5.4E-05	9.2E-05
	P50	1.5E-02	2.1E-02	5.4E-02	4.3E-02	5.2E-02	3.0E-05	1.6E-04	1.4E-04	2.0E-05	3.8E-05
	P75	2.9E-02	4.6E-02	1.2E-01	7.6E-02	9.2E-02	6.6E-05	3.8E-04	3.4E-04	4.4E-05	7.9E-05
	P95	7.7E-02	1.5E-01	3.9E-01	1.7E-01	2.1E-01	2.0E-04	1.4E-03	1.2E-03	1.3E-04	2.1E-04

Oils include vegetable and palm oils categories. Butter includes local and refined shea butter, and local and refined butter.
SD: Standard deviation. P50, P75 and P95: percentile 50th; 75th and 95th, respectively.

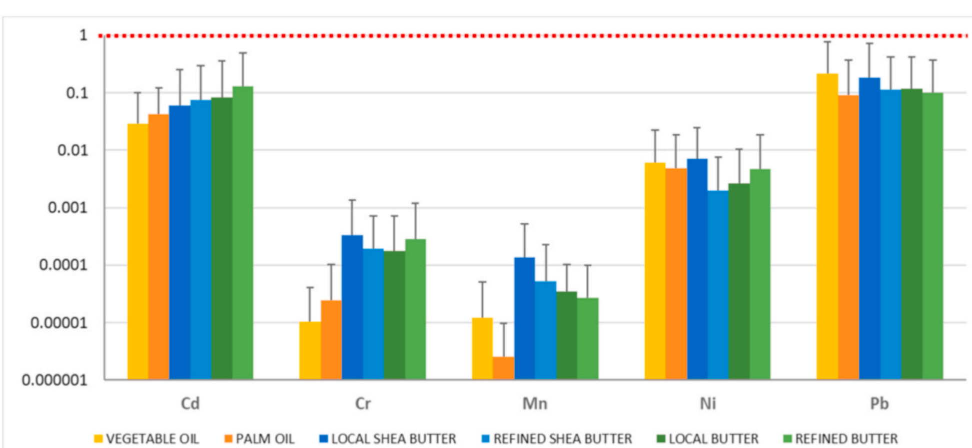

Fig. 5. Ratio between dietary intake and daily limit (tolerable daily intake for Cd, Cr and Ni, adequate intake for Mn, and BDML for Pb) of metals ingested through oil and butter consumption in the Delta Niger Region. Bars indicate 95th percentile.

butter, and a second cluster comprising vegetable oils and palm oils. It suggests that butter and shea butter samples presented a similar pattern of metal contamination and dissimilar from that of vegetable and palm oils. The local shea butter was distant from other samples by 25 units, presenting some similarity with refined shea butter.

The heat map reported in Fig. 4 did not reveal significant correlations between each metal and oil and butter samples, with the exception of Mn that strongly correlated with local shea butter, and in a less extent, with refined shea butter. This is in agreement with the high Mn concentration observed in shea butter samples (Table 1), as well as the results obtained by PCA and HCA (Figs. 2 and 3).

The dietary intakes of metals through oils and butter consumption and dermal cosmetic application are summarized in Table 4. Dietary intakes were more than twice orders of magnitude higher than dermal absorption for all metals, and for oil and butter categories. The tolerable dietary intakes set by the EFSA are 2.5 μg/kg/week (0.38 μg/kg/day), 300 μg/kg/day and 13 μg/kg/day, for Cd, Cr and Ni, respectively (EFSA, 2009, 2014, 2020). According to this, only the dietary intake of Cd was close to the respective limit. Mean Cd dietary intake through -exclusively- oil ingestion was below 5% of the tolerable daily intake (TDI). However, in case of exclusively butter ingestion, the mean dietary intake would mean between 6 and 13% of the TDI of Cd (Fig. 5). Taking into account the 95th percentile of Cd intake, it would mean between 19 and 37% of Cd TDI. An adequate intake (AI) of 3000 μg/kg/day was proposed for Mn by the EFSA (2013). Based on the present results, oils and butter seem not being relevant sources of Mn for the Niger Delta population (Fig. 4). Finally, regarding Pb, lowest benchmark doses (BMDL) were set at 0.5 or 0.63 μg/kg/day, for neurotoxicological development or chronic kidney disease, respectively (EFSA, 2010). Mean Pb intake through oils and butter were 17% and 13%, respectively, of neurotoxic effects BDML (0.5 μg/kg/day) (Fig. 5). Considering the 95th percentile of Pb intake, it means 49% and 37% of the BDML for the same effects, for an oil and butter -exclusively- consumption, respectively. It should be taken into account that these intakes were calculated using only oil/-butter consumption. Considering metal intake through consumption of other food categories, for example meat and fish, which were recently reported (Okoye et al., 2021a), the safety limits for Pb would be easily surpassed. Consequently, Cd, at least in 95th percentile of the dietary intake, and Pb intakes through oil and butter consumption, should not be considered negligible for human health protection in the Niger Delta Region under the current risk assessment.

4. Conclusions

The profile of heavy metals seems to be different for oil and butter samples. The first group would be mainly associated to high levels of Pb, while the second one to high concentrations of Cd, Cr, Mn and Ni. Shea butter was associated to high Mn content. In turn, Cd, Ni and Pb concentrations were over the international maximum allowable levels for these metals in some analyzed samples. The combination of univariate and multivariate data analysis was an efficient tool in researching the similarity and distribution of the analyzed metals in vegetable oils and butter, which should be very useful in order to assess the risks of dietary intake of metals for human health. Dermal absorption of metals, due the applications of oil and fats, was much lower than dietary intake. Metals ingestion through oils and fats by the Nigerian population here evaluated is not negligible taking also into consideration other food categories co-exposure.

Authors contribution

CNA: Data collection and bench work, BB and FR: Formal analysis & Manuscript writing, ANE and GU: Data collection and bench work, JLD, JR, CF: Formal analysis & Manuscript writing and OEO: Conceptualization & Manuscript writing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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