

1 **Human dietary exposure to metals in the Niger Delta**  
2 **Region, Nigeria: Health risk assessment**

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28 **ABSTRACT**

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30 The contamination profile and the human health risk assessment of various heavy metals  
31 (Cd, Cr, Mn, Ni and Pb) in vegetable oils, palm oils, butter and shea butter purchased  
32 from the Nigerian market were evaluated. Univariate and multivariate analyses including  
33 the principal component analysis (PCA), hierarchical cluster analysis (HCA) and heat  
34 map visualization were used to evaluate correlation, similarity and source of metals.  
35 Dietary intake and dermal absorption through the application in skin were also assessed.  
36 The heavy metals 5<sup>th</sup> and 95<sup>th</sup> percentile interval range (in mg/kg) were 0.003-0.208,  
37 0.003-0.392, 0.003-1.344, 0.003-0.369 and 0.006-0.531 for Cd, Cr, Mn, Ni and Pb,  
38 respectively. Concentrations of Cr and Mn were significantly different between sample  
39 category, being the levels of Mn and Ni positively correlated. The result of PCA, HCA  
40 and heat map revealed the profile of heavy metals in oils was different from that of butters,  
41 with Pb mainly associated to oils, and Cd, Cr, Mn and Ni to butters. In some samples, the  
42 international maximum levels for Cd, Ni and Pb in edible oils were exceeded. Cadmium  
43 and Pb dietary intake through Nigerian oils and butters should not be considered  
44 negligible for human health protection.

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47 *Keywords:* metals, oils and butters, dietary intake, dermal absorption, Nigeria

48

## 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 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 (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 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 is 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).

83 The deleterious effects of metals on the flavour and oxidative stability of oils should be  
84 also considered taking into account that some elements could catalyse oxidation of fatty  
85 acid chains, exerting a deleterious influence on shelf life and nutritional value (Galeano  
86 et al., 2006). The metal profile is subject to food legislation (Cypriano et al., 2008), and  
87 it is used for detecting adulterations in oils (González et al., 2010).

88 Metals such as Cd, Cr, Mn, Ni and Pb may negatively affect people's health.  
89 Cadmium is known to accumulate in human body and may induce kidney dysfunction,  
90 skeletal damage, and adverse reproductive effects (Forte et al., 2011; Oggiano et al.,  
91 2021). In turn, Cr is an essential nutrient for humans as it is involved in the glucose  
92 tolerance. Adequate Cr nutrition may reduce risk factors associated with cardiovascular  
93 disease, as well as diabetes mellitus. However, hexavalent Cr is potentially toxic and  
94 carcinogenic (Reilly, 2002). On the other hand, various studies identified that the  
95 deficiency of Mn can result in severe skeletal and reproductive abnormalities in  
96 mammals, while high doses of Mn produce adverse effects primarily on the lungs and on  
97 the brain (IPCS, 1999). With respect to Ni, trace amounts of this metal may be beneficial  
98 as an activator of some enzyme systems, but its toxicity at high levels can be prominent.  
99 Nickel may provoke allergies in particularly sensitive consumers. People suffering from  
100 a contact allergy to Ni may have been previously sensitized by the amounts of Ni present  
101 in food or drink (Cristaudo et al., 2019; Petrucci et al., 2019). Finally, Pb is a cumulative  
102 element that affects multiple body systems, including the neurological, haematological,  
103 gastrointestinal, cardiovascular and renal systems (Forte et al., 2011; Farace et al., 2021).  
104 In addition, Pb accumulates and substitute's Ca in bone tissues and the resultant effect is  
105 disruption of mineralization, alteration of compositional properties, and bone formation  
106 mechanisms (Gangoso et al., 2009).

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

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## 115 **2. Materials and methods**

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117        *2.1. Study area and sample collection*

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

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

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131        *2.2. Analysis of metals*

132        The concentrations of Cd, Cr, Mn, Ni and Pb in 43 oil and butter samples were  
133 determined. The analytical procedure was previously reported (Okoye et al., 2021a).  
134 Briefly, 5 g of each sample were digested in 9 mL of 65% HNO<sub>3</sub> (Merck, Darmstadt,  
135 Germany) and 3 mL of perchloric acid (Merck, Darmstadt, Germany) in a hot plate at  
136 110°C for 5 h. Afterwards, samples were introduced into an oven under a temperature  
137 that was gradually increased in 100°C every 60 minutes, until the requested final  
138 temperature of 450°C was reached. Finally, 18 h later, white ashes were obtained. After  
139 cooling, white ashes were dissolved in 5 mL of HNO<sub>3</sub> (1.5%) and make up to 25 mL with  
140 deionized water. The resulting solution was filtered using a Whatman filter paper (number  
141 42) fitted into a Buchner funnel, before being transferred into a tightly sealed plastic  
142 container. A GBC Sense AA 800G high-resolution continuum source atomic absorption  
143 spectrometer (SE-710690), coupled to graphite furnace (Cambridge CB5 8BZ,  
144 Cambridgeshire, UK), was used for metal analysis.

145  
146        *2.3 Quality Control*

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148        All chemical reagents and solvents used were of picograde quality. To achieve  
149 reproducible and reliable results, in the analyses of Cd, Cr, Mn, Ni and Pb, the instrument  
150 was recalibrated after every ten runs. The analytical procedure was checked using spike

151 recovery method (SRM). For it, a known standard of elements was spiked into already  
152 analyzed samples and reanalyzed. High purity multi-cathode lamp (1000 mg/kg) from  
153 Cambridge CB5 8BZ (Cambridgeshire, UK) was used to obtain the calibration curves for  
154 each metal. The multi-element calibration curves were verified with a multi-element  
155 certified material of 1000 mg/kg (Cambridge CB5 8BZ, Cambridgeshire, UK). The  
156 percentages of recovery varied between 94.5 and 100%. The relative standard deviation  
157 between replicate analyses was less than 4%. The limits of detection (LoD) were 0.001  
158 mg/kg for Cd, Cr, Mn and Ni, and 0.01 mg/kg for Pb, while the limits of quantification  
159 (LoQ) were 0.0033 mg/kg for Cd, Cr, Mn and Ni, and 0.033 mg/kg for Pb.

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#### 161 *2.4 Univariate and multivariate statistical analyses*

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163 The Kruskal-Wallis test was used to detect statistically significant differences  
164 between samples, while the Spearman' correlation analysis was employed to ascertain the  
165 interrelationships between the analyzed metals. A combination of Principal Component  
166 Analysis (PCA), hierarchical cluster analysis (HCA), and heat map were used for the  
167 multivariate analysis, and applied to the complete data set. In the PCA, the Varimax  
168 rotation extraction method with Kaiser normalization was used. Eigenvalues >1 were  
169 adopted as the significant benchmark for the principal components (PCs). Three PCs  
170 (PC1, PC2 and PC3) were above 1 in the data set, and hence, were extracted for further  
171 analysis. Afterwards, the PCs were represented by a coordinate axis projected in a three-  
172 dimensional graph (for the three PCs) for an easier spatial visualization of the data. In the  
173 HCA, the clusters were determined by the Ward's method and squared Euclidean  
174 measure, being shown in dendrograms. In addition, the two-dimensional heat map was  
175 composed with the colour map according to the correlation of each metal with samples.  
176 Statistical analysis was performed with the SPSS software, version 2020 (SPSS Inc.,  
177 Chicago, IL, USA).

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#### 179 *2.5 Estimated daily intake and risk assessment*

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181 Metal intakes through oil and butter consumption were calculated using equation  
182 (1), while dermal absorption due to application of oils and butters were calculated using  
183 equation (2). Dermal and dietary intake assessments were done probabilistically using  
184 Montecarlo simulation with the Oracle Crystal ball software (version

185 11.1.2.4.850). Propagation of variability and uncertainty were conducted using a  
186 probability function for each parameter and until reaching 100,000 iterations.  
187 Probabilistic approach in exposure and risk assessment is commonly used in exposure  
188 and risk assessment in order to solve data scarcity and uncertainty (Okoye et al., 2021a,b;  
189 Rovira et al., 2016).

190 
$$\text{Dietary intake} = \text{IR} \times \text{C} / \text{BW} \quad (1)$$

191 
$$\text{Dermal absorption} = \text{A}_p \times \text{C} \times \text{ABS} / \text{BW} \quad (2)$$

192 where Dietary intake is the intake of metals through consumption of oils and butter in  
193  $\mu\text{g}/\text{kg}/\text{day}$ ; IR is the ingestion rate of vegetable oil and butter (in  $\text{g}/\text{day}$ ); C is the  
194 concentration of metals in vegetable oils and fat (in  $\mu\text{g}/\text{g}$ ) obtained in present study; BW  
195 is the body weight ( $70 \pm 10.3$  kg) (Ihedioha et al., 2014). In turn, Dermal absorption is  
196 the absorption through the skin due to the application of oils and fats in the whole body  
197 and the lips (in  $\mu\text{g}/\text{kg}/\text{day}$ );  $\text{A}_p$  is the amount of oil or butter applied to the skin ( $8.69 \pm 5.09$   
198 g and  $0.024 \pm 0.034$  g for whole body and lips, respectively) (Loretz et al., 2005); ABS is  
199 the absorption rate for each metal (0.01, 0.002, 0.03, 0.008 and 0.003 for Mn, Ni, Cr, Cd,  
200 and Pb, respectively) (Lim et al., 2018). Since the data scarcity, IR of vegetable oils and  
201 butter was assumed to be  $29.4 \pm 4.3$  g/day, which is the mean ( $\pm$  standard deviation)  
202 obtained from studies conducted in Kenya, Nigeria and Spain (Iwegbue et al., 2021;  
203 Partearroyo et al., 2019; Steyn and Nel, 2006), as well as data from food supply from the  
204 Food and Agriculture Organization (FAO) (FAOSTAT, 2021). For C, BW and  $\text{A}_p$   
205 parameters, a logarithmic normal distribution was used. However, due to the lack of data,  
206 for IR and ABS a normal distribution was used.

207

### 208 **3. Results and discussion**

209

210 The levels of Cd, Cr, Mn, Ni and Pb in Nigerian oils and butters are shown in  
211 Table 1. The mean Cd concentration in samples ranged between  $0.025 \pm 0.019$  mg/kg in  
212 vegetable oils and  $0.115 \pm 0.113$  mg/kg in refined butter, with no significant ( $p > 0.05$ )  
213 differences between oil and butter categories (Figure 1a). The Codex Alimentarius for  
214 contaminants and toxins in food and feed has established a maximum level (ML) of 0.1  
215 mg/kg for Cd in edible vegetable oils (FAO, 2001). In the current survey, 19% (8 out 43)  
216 of the analyzed samples exceeded this limit. A previous study carried out in Abia State,  
217 South-eastern Nigeria (Nnorom et al., 2014), reported levels of Cd in palm oil of  
218  $0.064 \pm 0.020$  mg/kg, which are comparable to the levels of palm oil found in the present

219 study ( $0.037\pm 0.016$  mg/kg). In vegetable oils sold in Zaria (Northern Nigeria), the lowest  
220 and highest Cd values were 0.34 and 2.77 mg/kg, respectively (Ogabiela et al., 2010). In  
221 turn, in samples of edible vegetable oils produced in Iran, Cd was found to be 1.87–8.58  
222  $\mu\text{g}/\text{kg}$  (Farzin and Moassesi, 2014).

223 The levels of Cr were significantly different ( $p=0.007$ ) among oil and butter  
224 samples (Figure 1b), showing the lowest mean concentration in vegetable ( $0.007\pm 0.008$   
225 mg/kg) and palm ( $0.017\pm 0.023$  mg/kg) oils, and the highest in butter samples, with the  
226 maximum value detected in local shea butter ( $0.234\pm 0.291$  mg/kg). In previous  
227 investigations also conducted in Nigeria, the overall mean concentration of Cr in palm oil  
228 samples from Abia State was  $0.176\pm 0.048$  mg/kg (range 0.101-0.298 mg/kg) (Nnorom et  
229 al., 2014), which was higher than the levels found in Lagos (0.021-0.033 mg/kg)  
230 (Adepoju-Bello et al., 2012). Manganese presented lower levels in vegetable  
231 ( $0.084\pm 0.013$  mg/kg) and palm ( $0.017\pm 0.018$  mg/kg) oils than in butter, especially for  
232 local shea butter ( $0.945\pm 0.944$  mg/kg) and refined shea butter ( $0.370\pm 0.493$  mg/kg). As  
233 for Cr levels, Mn concentration was significantly ( $p=0.003$ ) different between sample  
234 categories (Figure 1c). In the current survey, Mn levels were lower than those previously  
235 reported in Nigerian palm oils (6.55-12.05 mg/kg) (Nnorom et al., 2014). However, they  
236 were more comparable with data from different varieties of vegetable oils purchased in  
237 China (from 0.113 mg/kg in olive oil to 0.556 mg/kg in peanut oil) (Zhu et al., 2011).

238 Concentrations of Ni in the present study ranged between 0.060 and 0.216 mg/kg  
239 in oils and butter, with no significant ( $p>0.05$ ) differences between sample categories  
240 (Figure 1d). According to international requirements, the content of Ni in oils should not  
241 surpass 0.2 mg/kg, while the 35% (15 out of 43) of the analyzed samples exceeded this value  
242 (Kowalewska et al., 2005). The Ni levels observed in the current study were higher than  
243 those reported in the scientific literature for Spanish (Llorent-Martínez et al., 2011) and  
244 Turkish edible oils (Pehlivan et al., 2008), but lower than those found in Nigerian oils  
245 (Nnorom et al., 2014; Adepoju-Bello et al., 2012; Ogabiela et al., 2010). In samples from  
246 China, the Ni content ranged between 0.026 mg/kg in peanut oil and 0.075 mg/kg in  
247 sesame oil (Zhou et al., 2011). Lead concentration ranges were 0.003-0.664 mg/kg in oils,  
248 0.014-0.315 mg/kg in butter ( $0.006\pm 0.582$  mg/kg in shea butter). No significant ( $p>0.05$ )  
249 differences were observed between the kinds of oils and butters (Figure 1e). The levels  
250 of Pb detected in the present survey were higher than those found in palm oils purchased  
251 from Lagos (0.022-0.038 mg/kg) and Abia State (0.024-0.067 mg/kg) (Adepoju-Bello et  
252 al., 2012; Nnorom et al., 2014). Notwithstanding, they were comparable to the levels

253 reported in vegetable oils (0.01-0.34 mg/kg) purchased from Zaria (Nigeria) (Ogabiela et  
254 al., 2010). Lower levels of Pb were detected in edible vegetable oils from Italy and  
255 Turkey, where concentrations ranged between 0.005-0.043 mg/kg and 0.04-0.11 mg/kg,  
256 respectively (Dug et al., 2004; Acar, 2012). Lead concentrations in edible vegetable oils  
257 were reported to be 0.028-0.064 mg/kg in China and 4.56-15.82 µg/kg in Iran (Zhu et al.,  
258 2011; Farzin and Moassesi, 2014). The Codex Alimentarius and the European legislation  
259 established a maximum of 0.10 mg/kg for Pb in oil and butters (FAO, 2001; EU  
260 Commission Regulation (EC), 2001). In the present study, around the 60% (23 out 43) of  
261 samples exceed that limit for Pb.

262 The results of the Spearman's correlation analysis (Table 2) showed the negative  
263 correlation between Cd and Mn ( $p < 0.05$ ), as well as the positive correlation between Mn  
264 and Ni ( $p < 0.05$ ) in oils (including vegetable and palm oils). In butter samples (including  
265 also shea butter), the only significant positive correlation was between Mn and Ni  
266 ( $p < 0.01$ ), as also observed in oils. Considering the whole data set (oil plus butter samples),  
267 no significant ( $p > 0.05$ ) correlations between metals were found.

268 The eigenvalues and variance of PCA applied to all samples of oils and butter are  
269 reported in Table 3. Based on PCA, the first three PCs explained 72.6% of the total  
270 variance. The PC1 explained up to 29.3% of the total variance, being characterized by  
271 high positive loadings of Cd (0.735), Mn (0.580) and Ni (0.765). The PC2 explained  
272 22.5% of the total variance, being dominated only by Pb (0.914). Finally, the PC3  
273 explained 20.8% of the total variance and was dominated by Cr (0.976). Figure 2 shows  
274 the three principal component plot, indicating that Cd, Mn and Ni were the most  
275 correlated metals. In turn, Cr and Pb formed a big angle with the other metals, confirming  
276 that there are no correlation between these metals and the remaining elements (Figure 2a)  
277 as previously found with Spearman's correlation analysis (Table 2). The PC1 component  
278 was better represented by butter than by oil samples, and across this component, the  
279 higher loadings were associated to Cd, Mn and Ni (Figures 2a and 2b). In particular, Cd  
280 appeared mainly associated to refined butter samples, presenting high concentration  
281 values (0.20-0.28 mg/kg) in three samples of margarine. Manganese was associated with  
282 various types of butter, with the highest values found in local and refined shea butter  
283 samples (interval 1.4-2.4 mg/kg). Some local shea butter samples, which showed higher  
284 Mn levels, presented also high Ni levels (0.25-0.50 mg/kg). On the other hand, PC2  
285 seemed to separate vegetable oil samples from the rest of the samples, being this PC  
286 component very influenced by the content of Pb (Figures 2a and 2b). Some vegetable oils

287 and one palm oil sample presented the highest Pb concentration in comparison to the  
288 others samples, which varied from 0.31 mg/kg in soya oil to 0.54 mg/kg in extra virgin  
289 olive oil. A slight separation between butter samples from oil samples was also observed  
290 across the PC3 component, which is mainly represented by Cr (Figures 2a and 2b). Butter  
291 samples presented more than 10-fold higher Cr concentration respect to that in oil samples  
292 as shown in Table 1.

293 HCA can be used as an alternative method to confirm PCA results and provide  
294 grouping of variables and samples. The HCA results for the heavy metals in samples are  
295 depicted in Figure 3. The dendrogram of Figure 3a shows that Cd, Ni and Pb formed one  
296 cluster, while Cr and Mn formed another cluster, independent of the others. Manganese  
297 was distant by 25 units, suggesting that this metal did not correlate with the remaining  
298 metals. Therefore, metals such as Cd, Ni and Pb, which were clustered in the same group,  
299 may come from the same source, while Cr and Mn may have a different origin. Regarding  
300 oil and butter samples (Figure 3b), two distinct clusters were observed, namely one cluster  
301 constituted by local butter, refined butter and refined shea butter and a second cluster  
302 comprising vegetable oils and palm oils. It suggested that butter and shea butter samples  
303 presented a similar pattern of metal contamination and dissimilar from that of vegetable  
304 and palm oils. The local shea butter was distant from other samples by 25 units, presenting  
305 some similarity with refined shea butter.

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

311 The dietary intakes of metals through oils and butter consumption and dermal  
312 cosmetic application are summarized in Table 4. Dietary intakes were more than twice  
313 orders of magnitude higher than dermal absorption for all metals, and for oil and butter  
314 categories. The tolerable dietary intakes set by the EFSA are 2.5 µg/kg/week (0.38  
315 µg/kg/day), 300 µg/kg/day and 13 µg/kg/day, for Cd, Cr and Ni, respectively (EFSA  
316 2009, 2014, 2020). According to this, only the dietary intake of Cd was close to the  
317 respective limit. Mean Cd dietary intake through -exclusively- oil ingestion was below  
318 5% of the tolerable daily intake (TDI). However, in case of exclusively butter ingestion,  
319 the mean dietary intake would mean between 6 and 13% of the TDI of Cd (Figure 5).  
320 Taking into account the 95<sup>th</sup> percentile of Cd intake, it would mean between 19-37% of

321 Cd TDI. An adequate intake (AI) of 3000 µg/kg/day was proposed for Mn by the EFSA  
322 (2013). Based on the present results, oils and butter seem not being relevant sources of  
323 Mn for the Niger Delta population (Figure 4). Finally, regarding Pb, lowest benchmark  
324 doses (BMDL) were set at 0.5 or 0.63 µg/kg/day, for neurotoxicological development or  
325 chronic kidney disease, respectively (EFSA, 2010). Mean Pb intake through oils and  
326 butter were 17% and 13%, respectively, of neurotoxic effects BDML (0.5 µg/kg/day)  
327 (Figure 5). Considering the 95<sup>th</sup> percentile of Pb intake, it means 49% and 37% of the  
328 BDML for the same effects, for an oil and butter -exclusively- consumption, respectively.  
329 It should be taken into account that these intakes were calculated using only oil/butter  
330 consumption. Considering metal intake through consumption of other food categories, for  
331 example meat and fish, which were recently reported (Okoye et al., 2021a), the safety  
332 limits for Pb would be easily surpassed. Consequently, Cd, at least in 95<sup>th</sup> percentile of  
333 the dietary intake, and Pb intakes through oil and butter consumption, should not be  
334 considered negligible for human health protection in the Niger Delta Region under the  
335 current risk assessment.

336

#### 337 **4. Conclusions**

338

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

350

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

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

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SD: Standard deviation. P5 and P95: percentile 5<sup>th</sup> and 95<sup>th</sup>, respectively

528 **Table 2. Spearman's correlation matrix of metals in Nigerian oils and butters**  
 529

<b>Samples</b>		<b>Cd</b>	<b>Cr</b>	<b>Mn</b>	<b>Ni</b>	<b>Pb</b>
<b>Oils</b>	<b>Cd</b>	1				
	<b>Cr</b>	-0.020	1			
	<b>Mn</b>	<b>-0.556*</b>	0.252	1		
	<b>Ni</b>	0.032	0.176	<b>0.462*</b>	1	
	<b>Pb</b>	0.236	-0.158	-0.392	-0.402	1
<b>Butter</b>	<b>Cd</b>	1				
	<b>Cr</b>	-0.151	1			
	<b>Mn</b>	0.177	-0.079	1		
	<b>Ni</b>	0.400	0.057	<b>0.525**</b>	1	
	<b>Pb</b>	0.046	-0.015	0.135	0.353	1
<b>Oils and Butter</b>	<b>Cd</b>	1				
	<b>Cr</b>	-0.023	1			
	<b>Mn</b>	0.057	0.291	1		
	<b>Ni</b>	0.278	-0.155	0.244	1	
	<b>Pb</b>	0.135	-0.135	-0.137	0.034	1

530 Oils include vegetable oils and palm oil categories. Butter includes local and refined shea butter,  
 531 and refined and local butter

532 \*p<0.05; \*\*p <0.01

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535 **Table 3. Eigenvalues and variance of Principal Component Analysis (PCA) of**  
 536 **metals in oils and butter samples**  
 537

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

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

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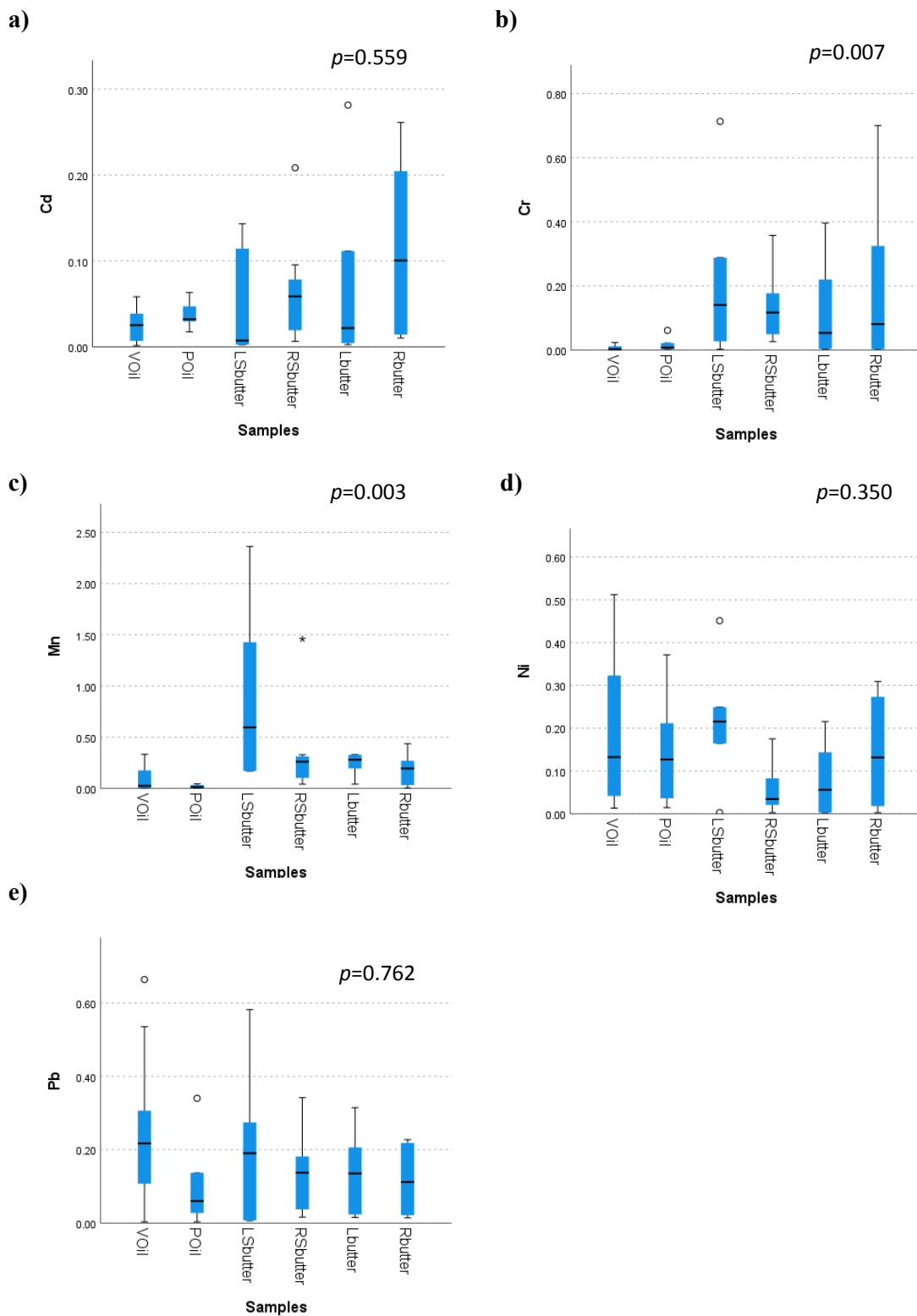
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**Table 4. Dietary intake and dermal absorption ( $\mu\text{g}/\text{kg}/\text{day}$ ) of metals in oils and butters from the Nigerian market**

		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	1.1E-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	1.2E+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

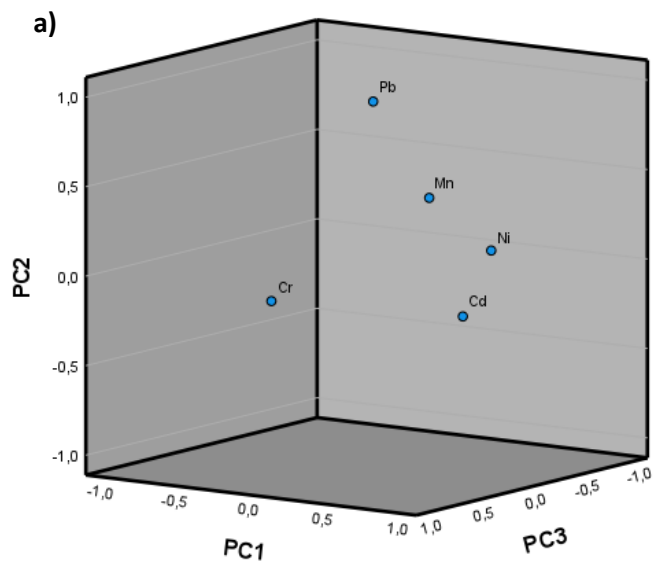
Oils include vegetable and palm oils categories. Butter includes local and refined shea butter, and local and refined butter.  
SD: Standard deviation. P50, P75 and P95: percentile 50<sup>th</sup>, 75<sup>th</sup> and 95<sup>th</sup>, respectively

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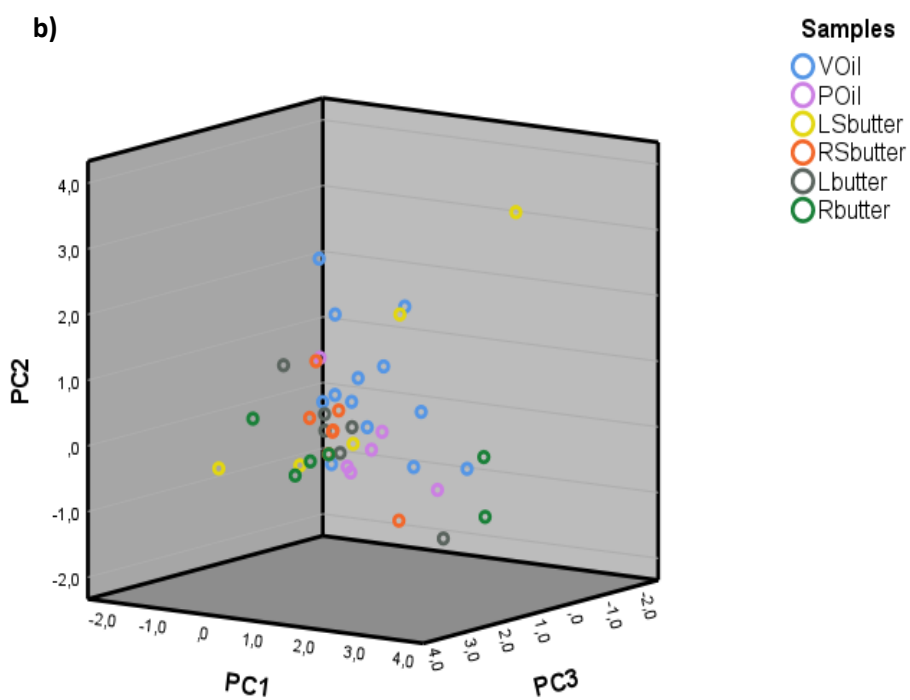


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Figure 1. Metals (a: Cd; b: Cr; c: Mn; d: Ni; e: Pb) levels in samples of oils and butters from the Nigerian market (VOil: vegetable oils; POil: palm oil; LSbutter: local shea butter; RSbutter: refined shea butter; LS: local butter; Rbutter: refined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



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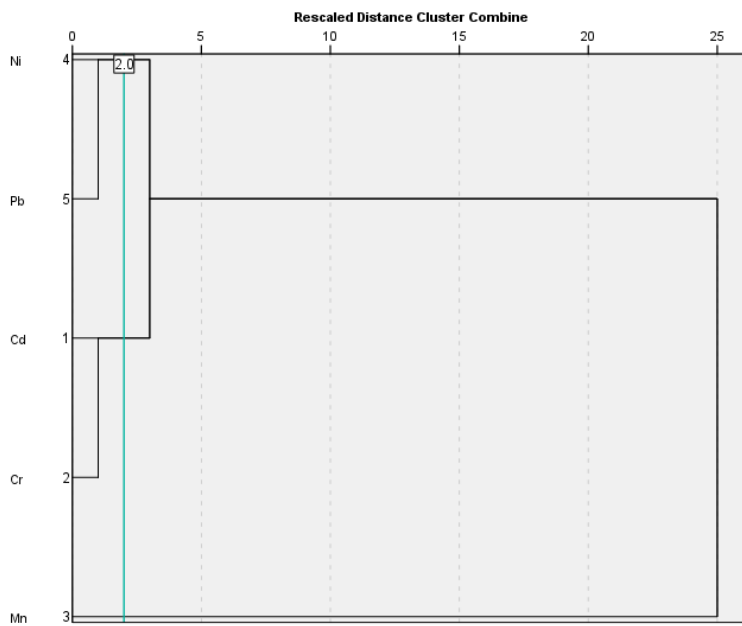
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Figure 2. Principal Component analysis (PCA) with Varimax rotation method of metals in sample of oils and butter: a) component plot by variables (metals); b) component plot by samples (VOil: vegetable oils; POil: palm oil; LSbutter: local shea butter;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

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a)



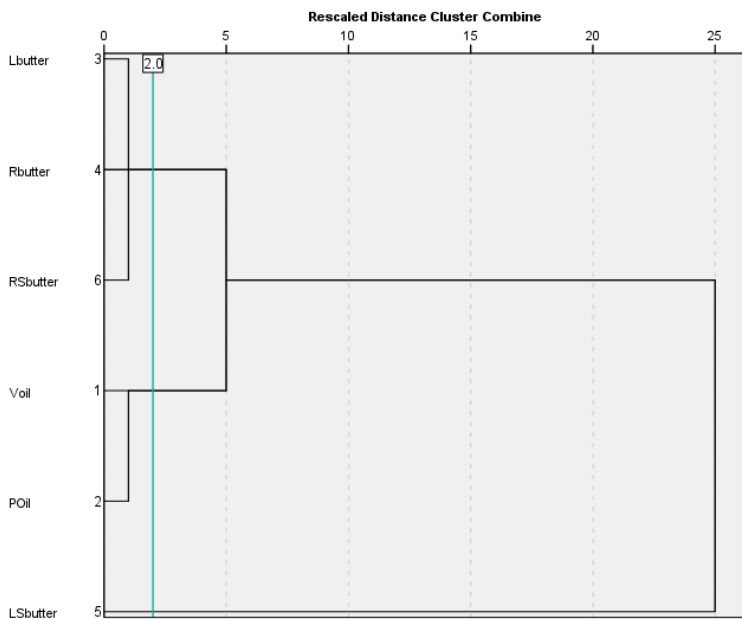
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b)



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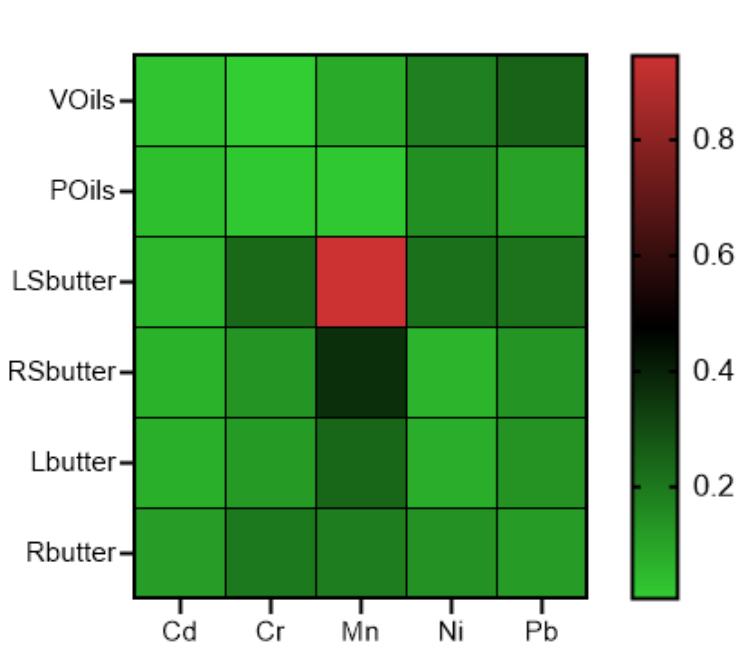
576 Figure 3. Hierarchical cluster analysis (HCA) using Ward's method and squared  
577 Euclidean measure of metals in oils and butter: a) cluster by variables (metals); a) cluster  
578 by samples (VOil: vegetable oils; POil: palm oil; LSbutter: local shea butter; RSbutter:  
579 refined shea butter;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

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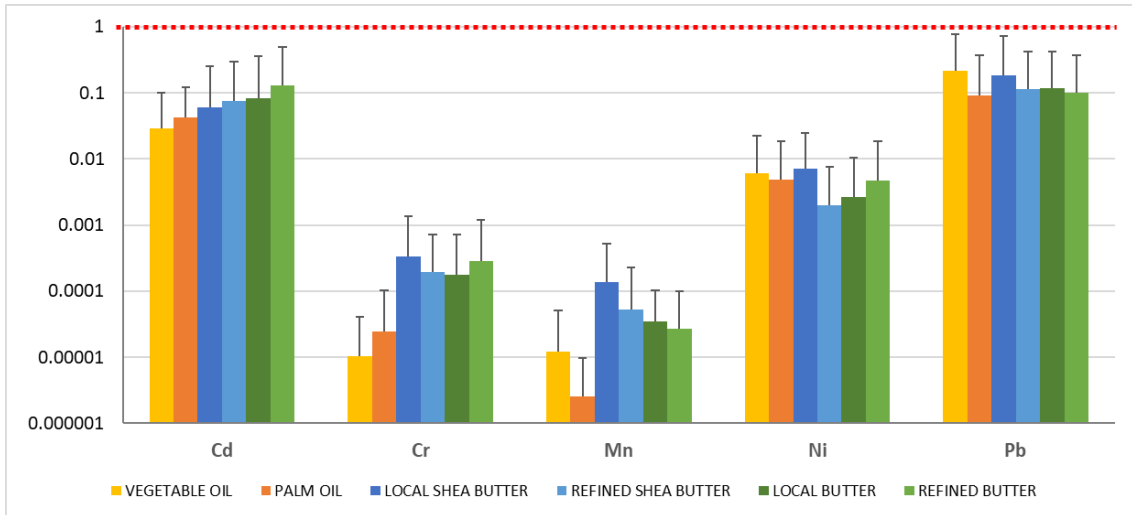
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Figure 4. Heat map of correlation for metals in oils and butter (VOil: vegetable oils; POil: palm oil; LSbutter: local shea butter; RSbutter: refined shea butter; LS: local butter; Rbutter: refined butter). Red: strong positive correlation; green: weak correlation.



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