

1 **Evaluation of the Concentrations of some heavy metals(Pb, Cd and Cr) and long term**
2 **exposure due to daily Consumption of ready-to-eat foods sold at Petrol station's**
3 **Atmospheric conditions (AF) in Calabar Metropolis.**
4
5

6 **Abstract**

7 **Background:** Heavy metals contamination has been reported at petrol station environments.
8 There is a possibility of contamination foods around petrol stations.

9 **Objectives:** In this study, the concentrations of Pb, Cd and Cr, long term exposure and daily
10 consumption of ready-to-eat food foods sold at Petrol station's Atmospheric conditions (AF) in
11 Calabar Metropolis was evaluated.

12 **Methods:** Foods samples, including such prepared ready-to-eat foods were collected at the point
13 of sale at the fuel stations, about 7:00am in the morning before they were opened for sale (and
14 exposed to the environment of the filling stations). These were labelled "Before". At about
15 2:00pm to 3:00pm same day, the same ready-to-eat food samples were collected again at the
16 same spots.

17 **Results:** In this study, the levels of Pb, Cd and Cr were determined in some ready-to-eat foods
18 that are sold around the filling station environments in Calabar metropolis. The results obtained,
19 as presented in Figures 1-3, showed that the levels of Pb and Cd were significantly ($p<0.05$)
20 increased in garri, afang soup, melon soup, white rice, beans, stew and meat pie, while the level
21 of and Cr was significantly ($p<0.05$) increased in afang soup, melon soup, white rice, beans, stew
22 and meat pie after 6 hours of exposure to petrol station's atmospheric conditions.

23 **Conclusion:** From this study, it may be concluded that exposure of ready-to-eat foods at the
24 filling station's atmospheric conditions may cause heavy metal contamination to the foods,
25 particularly Pb, Cd and Cr.

26 Key words: lead, Cadmium, Chromium, contamination and petrol stations
27

28 **Introduction**

29 Ready-to-eat foods are those foods that are considered to be ready to consume instantly at the
30 point of sale. Clarence *et al.* (2009) and Mahakarnchanakul *et al.* (2010) reported that these
31 foods may be consumed in either raw or cooked form, hot or cold as well as consumed with or
32 without further heat treatment. As reported by Tambekar *et al.* (2008) ready-to-eat foods on the
33 street are relatively cheap and readily accessible, accounting for the commonly available feeding
34 source for many city dwellers. Hence, street foods play important roles in the feeding pattern of
35 different categories of people in major urban cities in developing countries. It has been reported
36 that about 80% of Thai ready-to-eat foods are generally eaten uncooked and are exported to USA
37 and Europe (Jocelyn and Naewbanji, 2005). The ready-to-eat foods sold by food vendors and

38 hawkers in streets and other public places usually have high patronage probably due to
39 convenience, nutritional quality and flavor of the food. The sale of these foods helps to provide
40 the needed source of income for the non-skilled people in such cities, thereby contributing to
41 economic development of countries where such activities take place.

42 According to the FAO/WHO (2007), street foods may be obtained from a street side
43 vendor, often from a makeshift stall which could also be portable. Generally, certain appealing
44 factors that make street foods popular as food sources in most cities in the developing countries
45 include familiarity, organoleptic property of the food, low cost and convenience in getting the
46 food (Mahakarnchanakul *et al.*, 2010). There exists a social pattern characterized by increased
47 mobility, large number of itinerant workers and less family or home centered activities in
48 developing societies where these foods are sold. This situation, has led to an increase to the
49 increase in the amount of ready-to-eat foods taken outside the home. This therefore has led to the
50 proliferation of food vendor services with the responsibility of good manufacturing practices of
51 food being “transferred from individuals/families to the food vendors who usually do not enforce
52 such practices” (Musa and Akande 2002; Clarence *et al.*, 2009). In Nigeria, storage of these food
53 products is done under poor hygienic conditions. More often than not, the products are displayed
54 in open trays in open market places as well as hawked along the street by hawkers.
55 Contamination of food may occur at any point in the production chain (i.e. from the point of
56 harvest and transport of the raw materials, processing of the raw products, packaging,
57 transportation of finished product, storage and marketing) to the final point of consumption. Due
58 to poor processing methods used, these foods could therefore be contaminated by micro-
59 organism, heavy metals and pesticides. Data regarding metallic concentration of food products at
60 the point of consumption is necessary to allow for estimation of human exposure to these metals
61 (Iwegbue, 2011).

62 Basically, Governments and many government agencies globally are known to have
63 initiated several attempts to improve food safety, but food borne illnesses arising from food
64 contamination is reported to still possess a significant health threat to humans in both developed
65 and developing countries (Gasaluck, 2012). The ready-to-eat foods sold along streets are
66 considered to be of risk to public health as a result of the difficulty associated with the control of
67 quality of large number of street food vending operations. This difficulty is reported to be
68 attributed to the diversity of the food, food mobility and the temporary nature of the process as

69 well as inadequate basic infrastructure and services (Ghosh *et al.*, 2007; DeSausa, 2008). Foods
70 may be contaminated by the introduction of finely dispersed particles in the atmosphere into
71 foods. Entry of these finely dispersed particles into foods may occur mainly due to the
72 preparation and pre/post processing method used, wear and tear of metallic cooking vessels as
73 well as environmental pollutants.

74 The levels of metal content in foods is of great importance because of the huge role that
75 metallic ions play in health and disease (Hague *et al.*, 2008). The human body cannot tolerate
76 certain metals (like Cadmium and lead) at even low concentrations due to the fact that they are
77 highly toxic (Suppin *et al.*, 2006). Heavy metals may cause toxic responses by displacing a
78 physiologically appropriate metal. For example, “cadmium can replace copper and iron in
79 cytoplasmic and membrane proteins, with the free metal ions promoting the generation of free
80 radicals (superoxide and hydroxyl radical) which in turn can lead to oxidative damage of lipids,
81 nucleic acids and proteins” (Marias & Blackhurst, 2009). Cadmium has been implicated in the
82 development of skeletal damage (Jarap, 2003). Cadmium and lead have been reported to harm
83 reproductive system and embryonic development.

84 The physiologic roles of essential metals have been well documented. For example, Iron
85 (plays the role as a haemopoietics of hemoglobin and cytochromes) (Marias & Blackhurst 2009).
86 The physiologic roles of essential metals are due to the fact that these metals are constituents of
87 proteins. A deficiency of these elements could induce disease conditions. For example, a
88 deficiency of copper could induce elevated blood pressure, induce hypercholesterolemia and
89 increase low density lipoprotein content in the blood which could trigger cardiac arrest.
90 Similarly, a deficiency of manganese could cause chronic diseases like osteoporosis and diabetes
91 mellitus. Intake of essential metals above threshold limits could cause toxicity problems.
92 Epidemiological data have shown that there is a correlation between excessive dietary intake of
93 zinc and an increased prevalence of obesity and other related diseases (Singh & Taneja, 2010).

94 As in Nigeria and many other countries, ready-to-eat foods account for a significantly large
95 proportion of the daily food intake of individuals and families. A survey of revealed that only a handful of
96 literature exists for the content of metals in Nigerian foods and these studies are limited in scope with
97 respect to the type of element and food surveyed (Iwegbue, 2011). For example, Onianwa *et al.* (2001)
98 examined the levels and daily intake of Cu and Zn from confectioneries (sweets, biscuits and breads).
99 Currently, there is insufficient information regarding elemental composition of ready-to-eat foods
100 consumed in southern Nigeria and no real study on individual and combined target hazard quotient values

101 for common confectioneries has been reported, this study therefore seeks to provide a comprehensive
102 evaluation of the concentrations, daily intake and long term exposure to metals due to consumption of
103 ready-to-eat foods with a view to provide valuable information on the risks associated with their
104 consumption.

105

106 **Materials and Methods.**

107 **Materials**

108 The following equipment and glass wares were used in the course of this research:
109 Laboratory mortar (model EW-63100-60, from Cole-parmer company Ltd, USA), Evaporating
110 plate (model SER-No.62, from Gallenkamp company Ltd, UK), Atomic Absorption
111 Spectrophotometer (model AA6800, Schemadzu company, Japan).

112 **Reagents/chemicals**

113 Standard reagents and chemicals were used and include: Lichens coded International
114 Atomic Energy Agency (IAEA-336), from Sigma, USA, Nitric acid (Riedel-deHaën, Germany),
115 Perchloric acid (Sigma-Aldrich, Germany), Hydrofluoric acid, Ethanol, Methanol, Ethyl-acetate,
116 (British Drug House Chemicals Ltd, Poole, England), distilled deionized water (obtained from
117 Cross River State water board, Calabar-Nigeria).

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119

120 **Methods**

121 **Collection of food samples**

122 Foods samples, including such prepared ready-to-eat foods as garri, meat pie, stew, rice,
123 beans, afang and melon soups were collected at the point of sale at the fuel stations, about
124 7:00am in the morning before they were opened for sale (and exposed to the environment of the
125 filling stations). These were labelled “Before”. At about 2:00pm to 3:00pm same day, the same
126 ready-to-eat food samples were collected again at the same spots (after they have been exposed
127 to the filling stations atmospheric environment). These were labelled “After”. The food samples
128 were collected in such a way that all the Garri purchased before, across the different filling

129 stations were mashed together as a single sample, while the ones purchased after were equally
130 collected to form a single sample. The other food samples were handled in in like manner.

131 **Preparation of food samples for heavy metal analysis**

132 One gram (1.0g) each of the pulled samples was weighed into a beaker. 20ml of aqua-
133 rega (a solution of Nitric acid and perchloric acid (3:1) was added and the beaker was covered
134 with glass for the initial effervescence to subside. Thereafter, the beaker was placed on a hot
135 plate and heated to near dryness at about 80-90⁰C. The aqua-rega was added as required in the
136 course of digestion, to avoid drying. After the sample was fully digested, giving light coloured
137 solution, the beaker was transferred onto a work bench and allowed to cool. The cooled sample
138 was filtered into a 50ml beaker and made up to the mark with distilled water. This was
139 transferred into a sample container in preparation for heavy metal (elemental) determination
140 using Atomic Absorption Spectrophotometer (Awofolu, 2005).

141 **Analytical Quality Assurance**

142 To make sure that the analytical methods used for heavy metal determination are
143 reliability, standard reference materials, Lichens coded (International Atomic Energy Agency;
144 IAEA-336) were also digested and then analyzed using same procedure. Comparison of
145 determined values with certified elemental values was carried out to ensure reliability of the
146 analytical method used (Udiba *et al*, 2012).

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148

149

RESULTS

150 **Results showing the different concentrations of Pb, Cd and Cr in some ready-to-eat meals**
151 **before and after 6 hrs of exposure to petrol station's atmospheric conditions (AF)**

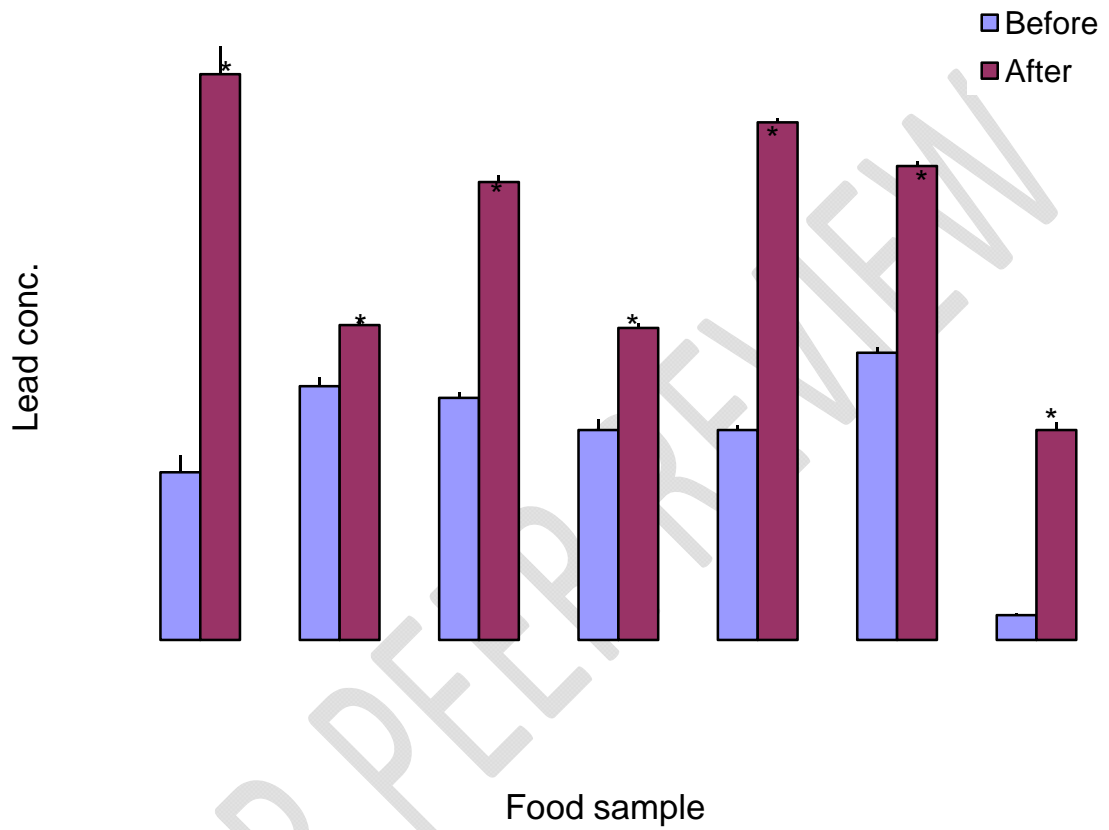


Figure 1: Comparison of concentration of lead before and after exposure in the different food samples.

Values are expressed as mean + SEM, n = 3.

* = significantly different from before exposure at $p < 0.05$

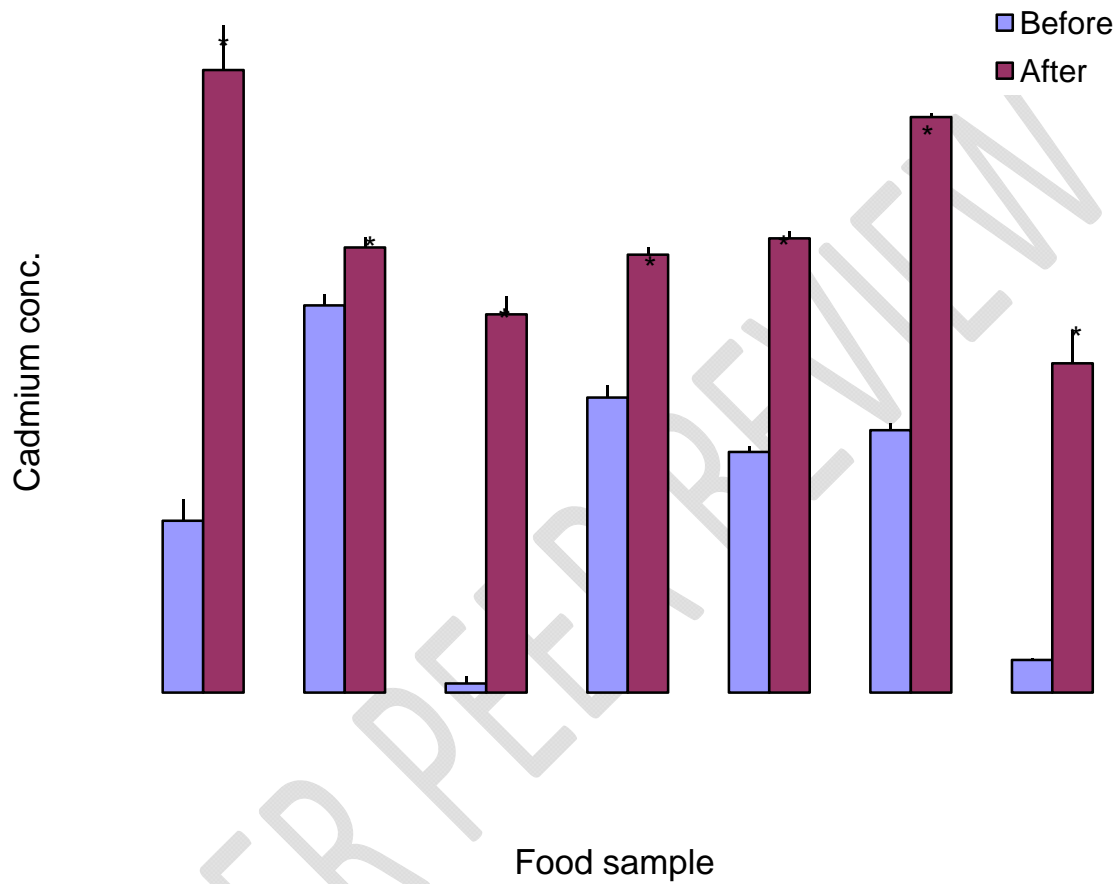


Figure 2: Comparison of concentration of cadmium before and after exposure in the different food samples.

Values are expressed as mean + SEM, n = 3.

* = significantly different from before exposure at p < 0.05

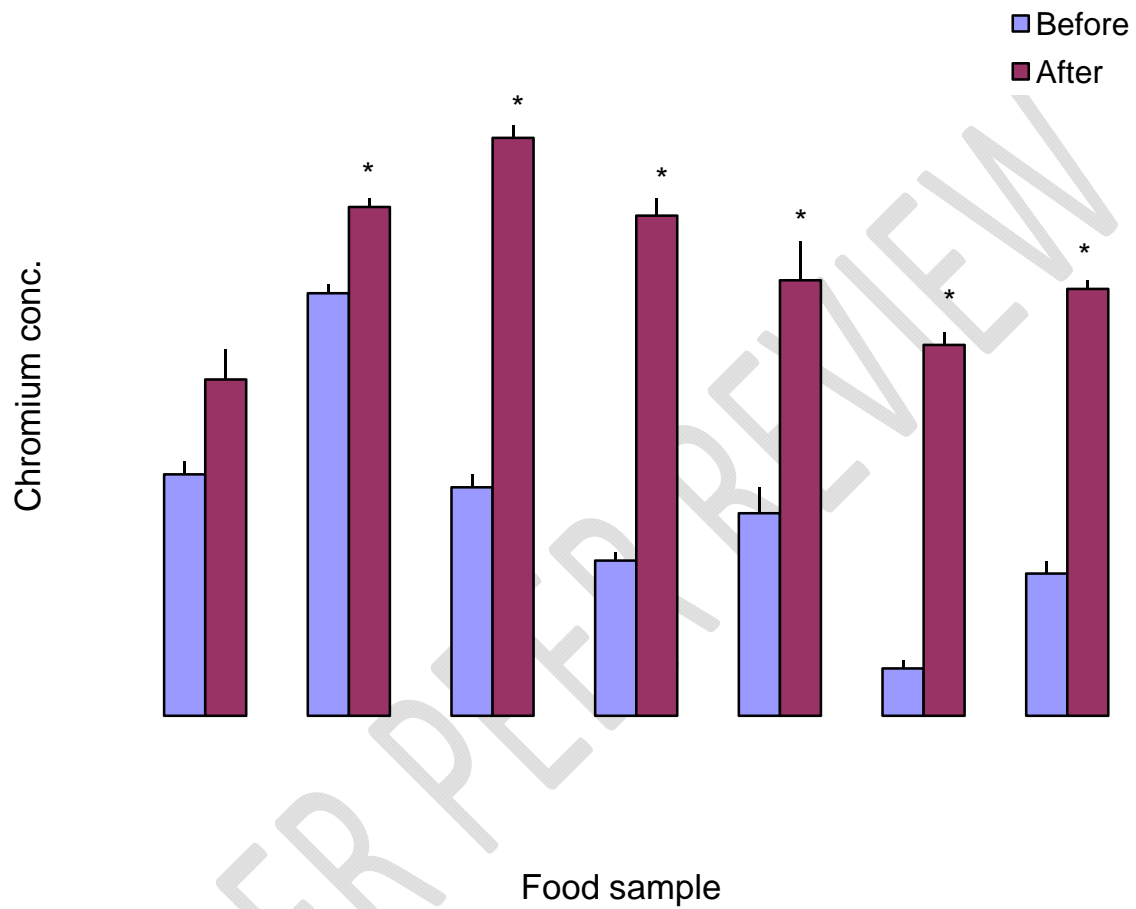


Figure 3. Comparison of concentration of chromium before and after exposure in the different food samples.

Values are expressed as mean + SEM, n = 3.

* = significantly different from before exposure at $p < 0.05$

155 In this study, the levels of Pb, Cd and Cr were determined in some ready-to-eat foods, including
156 garri, afang soup, melon soup, white rice, beans, stew and meat pie that are sold around the
157 filling station environments in Calabar metropolis. The results obtained, as presented in Figures
158 1-3, showed that the levels of Pb and Cd were significantly ($p < 0.05$) increased in garri, afang
159 soup, melon soup, white rice, beans, stew and meat pie, while the level of and Cr was
160 significantly ($p < 0.05$) increased in afang soup, melon soup, white rice, beans, stew and meat pie
161 after 6 hours of exposure to petrol station's atmospheric conditions. This shows that there is high
162 possibility of contamination of most of the ready-to-eat foods sold around the petrol stations
163 evaluated with heavy metals (such as lead, Cadmium and Chromium).

164 **Discussion**

165 The presence of heavy metals contaminants in foods has been a serious concern in most societies
166 of the world in recent times. Generally, increased exposure to heavy metal contaminants
167 introduced into the air from industrial activities and traffic congestion is a consequence of
168 advancement in industrialization. Exposure of food and food substances to heavy metals
169 contaminated environments is likely to result in the contamination of such food substances with
170 heavy metals. The petrol stations environment is among the areas reported to be characterized by
171 heavy metal contaminations (Dauda & Odoh, 2012; Afrifa *et al.*, 2013). The presence of heavy
172 metals in the air, water and food forms a major health threat globally (Matthew *et al.*, 2002).
173 Such human activities as use of agricultural pesticides, increase in industrialization and mining
174 are known to release high amount of heavy metals into the environment, thereby increasing the
175 levels of heavy metal pollution in the ecosystem (Srikanth *et al.*, 2004). Consumption of food
176 items displayed at these environments is therefore likely to expose the consumers to the risk of
177 these heavy metals toxicity. Some heavy metals are known to cause various health hazards to
178 individuals that consume those foods that are enormously contaminated with the metals.
179 Generally, heavy metals get into human systems following consumption of foods and drinking of
180 water that are contaminated with heavy metals. This study is therefore important in determining
181 the possibility of dietary consumption of heavy metals from food sources. This may also play a
182 key role in evaluating food safety and the consequent effects of heavy metals on the consumers.

183 This study assessed the level of some heavy metals in ready-to-eat foods such as prepared
184 garri, meat pie, stew, rice, beans, afang and melon soups that are sold at the petrol refueling

185 stations in Calabar. It was observed from the results of this study showed that petrol refueling
186 stations atmosphere, introduced high levels of Pb and Cd into garri, afang soup, melon soup,
187 white rice, beans, stew and meat pie sold within premises of the refueling stations. Also, high
188 level of Cr was recorded in garri, afang soup, melon soup, white rice, beans, stew and meat pie at
189 the petrol stations in Calabar, compared to the level recorded for the freshly prepared foods.
190 According to the “Joint FAO/ World Health Organization Expert Committee on Food Additives
191 (JEFCA) the established provisional tolerable weekly intake for lead is 0.025 mg/kg body
192 weight” (JEFCA, 2004). Also, the report of “WHO provisional guideline records 0.01 mg/L as
193 the adopted standard for drinking water” (WHO, 2004). According to the FAO/WHO standard,
194 “the permissible level of cadmium and lead is 0.05 and 0.2mg/kg, respectively”.

195 The level of these heavy metals, particularly Pb, Cr and Cd, were observed to be higher
196 than the World recommended limits. The observed increase in heavy metals contents in ready-to-
197 eat foods at the petrol stations implies that the atmospheric environment of petrol stations in
198 Calabar must have been contaminated with these heavy metals, from where they are likely
199 introduced into these food items. Reem *et al.*, (2012) reported that the level of Pb in some brands
200 of chicken liver meat sold in open market in Iraq is higher than the permissible limits. This
201 suggested the possibility of the introduction of Pb from a contaminated open market atmosphere
202 into the meat. Results of the current study gives a clear indication that most ready-to-eat foods
203 sold around the petrol stations may be prone to contamination with heavy metals (such as Pb, Cd
204 and Cr). The results of this study therefore support the report of Dauda & Odoh (2012) and
205 Afrifa *et al.* (2013), that the level of atmospheric air within the petrol refueling stations in South
206 South region of Nigeria are heavily contaminated with heavy metals. Also, Thirulogachandar *et*
207 *al.*, (2014) reported that the presence of heavy metals in poultry liver meat correlates the extent
208 of contamination due to water, foodstuff, air and premixes intake by the chicken.

209 The results of this study are in agreement with work done by Oladimeji *et al.* (2014) that
210 who reported that ready-to-eat foods at traffic and industrial activities congested areas contain
211 high level of such heavy metals as Cd, Pb and Cr. Since the concentrations of Pb, Cd and Cr in
212 the ready-to-eat foods in this study were high, it can be deduced that consumption of these foods
213 may pose a significant health hazard to their consumers. In a study carried out by Sharma *et al.*
214 (2009), “a concentration of 1.96 mg/kg was recorded for cadmium in tomatoes collected from
215 production and market sites of a tropical urban area of India”. Similarly, high amounts of

216 cadmium was been reported by Jimoh *et al* (2012). However, the studies carried out by Radwan
217 & Salama (2006) in Egypt reported a concentration of 0.01 ± 0.00 mg/kg of Cd (i.e., below the
218 standard threshold) in some Egyptian fruits and vegetables, including tomatoes. Since the level
219 of Cd recorded in this study for ready-to-eat foods was above the reported tolerable limits,
220 consumption of these foods may pose a health risk to the consumers, as observed by Zheng *et al.*
221 (2007).

222 A study on heavy metal content of Egyptian fruits and vegetables reported the
223 concentration of 0.26 ± 0.09 mg/kg (Radwan & Salama, 2006), while Aryan Dermisbas (2009)
224 reported Pb concentration of 0.43 ± 0.08 mg/kg for tomatoes from market survey in Egypt. It has
225 been reported that the presence of lead in foodstuff at a concentration higher than the maximum
226 permissible limit of 0.2 mg/kg can pose both long and short term health hazard (Oladimeji *et al.*,
227 2014). According to this report, “short-term exposure to high levels of lead can cause brain
228 damage, paralysis (or lead palsy), anaemia and gastrointestinal symptoms”. Consumption of
229 foods containing high concentration of lead may therefore pose a major health challenge(s) to the
230 consumers. Short-term exposure to low amounts of lead has been reported to produce adverse
231 effects on neuro-behavioral development of particularly young children (Food Safety Authority
232 of Ireland, 2009). The results obtained from this present research work suggest that the
233 consumption of ready-to-eat foods exposed to petrol stations environment for 8hours are liable to
234 cause lead toxicity.

235 The potential health risks that are known to be associated with exposure to heavy metals
236 in foods have attracted the concern of researchers in recent times. Literature reports clearly
237 pointed out that heavy metals are dangerous due to their non-biodegradability property and long
238 biological half lives, hence their ability to bio-accumulate within living tissues (Jarup, 2003;
239 Sathawara *et al.*, 2004; Banerjee *et al.*, 2011). According to Demirezen & Uruc (2006),
240 consumption of foods contaminated with heavy metals pose a serious health threat to the
241 consumers due to their toxicity effects, bioaccumulation and biomagnifications in food chains.
242 Although it may be difficult to prevent the contamination of the atmospheric air around
243 industrialized areas with heavy metals, it is important that strict measures of controlling the
244 exposure of food items to these contaminated environments should be devised and adopted.
245 Among these measures may include prevention of exposure and sale of ready-to-eat foods in
246 such open contaminated environments as petrol refueling stations. With this, the prevalence of

247 food contamination with heavy metals will be reduced, and the rate of consumption of heavy
248 metals contaminated foods will also be reduced.

249 **Conclusion**

250 From this study, it may be concluded that exposure of ready-to-eat foods at the filling station's
251 atmospheric conditions may cause heavy metal contamination to the foods, particularly Pb, Cd
252 and Cr. It is therefore advisable to protect the ready-to-eat foods sold within and around the
253 filling stations from direct exposure to the atmospheric conditions of the filling stations.

254

255 **COMPETING INTERESTS**

256 Authors have declared that no competing interests exist.

257

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