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1 **Parameters influencing the migration of trace metals in uncoated fruit cans**

2 *Running title: Migration of metals in uncoated fruit cans*

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11 **Abstract**

12 The migration of 8 trace elements (Fe, Sn, Cr, Cd, Pb, Ni, Cu and Zn) was monitored for
13 fruits canned in uncoated tinplate cans under different storage conditions until the shelf life.
14 The levels of most of these elements significantly increased with storage time and were also
15 affected by storage temperature. Particularly, storage at 40°C (simulating sunlight exposure
16 of the cans) caused important release of Sn and Fe so that canned foods did not comply with
17 regulation. Can denting accelerated the migration of several metals, especially Fe and Sn.
18 Moreover, Fe and Sn levels drastically increased in fruits kept in open cans stored in the
19 fridge for a few days. Small pieces of fruits contained higher level of metals than larger ones,
20 and the side seam coating reduced the migration of trace elements.

21 **Keywords:** canned fruits; migration; storage conditions; trace metals; uncoated cans

22

23 **Practical applications**

24 Canned fruits are a convenient alternative to fresh fruits to fulfil the nutritional
25 recommendations for a healthy diet. In the same time, canned fruits may be contaminated by
26 several trace metals (particularly tin, lead and chromium), partly due to their migration from
27 the unlacquered tinfoil cans. This study investigates several parameters prone to affect
28 metals migration during fruit cans handling and storage (storage time and temperatures,
29 denting the cans, leaving open cans in the fridge, as well as food brand and fruit type). Proper
30 advices for handling and storing canned fruits are proposed, especially since the low pH and
31 small pieces of fruits may favour metals release and uptake by the food.

32 **Introduction**

33 The daily consumption of fruits is nutritionally advisable. Yet, for some population fresh
34 fruits may be cumbersome to obtain due to remote locations or expensive costs. Canned fruits
35 are considered as a convenient alternative, and dietary advice to increase fruit consumption
36 include them as options in a healthy diet. In the same time, canned foods have been reported
37 to be significant contributors to human exposure to several trace metals (particularly tin, lead
38 and chromium) since, beyond their presence in the food raw material, they may migrate from
39 the cans during the canning process and their storage (Arvanitoyannis & Kotsanopoulos,
40 2014; Raptopoulou *et al.*, 2014). So, there is concern about the possible consumer exposure
41 to trace metals through canned fruits that are frequently produced and stored in tinfoil cans,
42 and epidemiological results raise questions about the evidence underlying dietary
43 recommendations to promote tinned fruit consumption as part of a healthy diet (Aasheim *et*
44 *al.*, 2015). In particular, a recent study reported elevated Sn levels in urine collected from
45 children in Korea (reaching up to 3 mg Sn/day for some children), and this was suspected to
46 be related to consumption of tin-canned foods and beverages, especially canned fruits (Yang

47 et al., 2015). Similarly, the second French diet study conducted few years ago revealed that
48 canned fruits contained the highest levels of Sn (up to 8.55 mg/kg) (Millour *et al.*, 2012).

49 Tinplate has a multi-layered structure (the basic material is low-carbon steel plate, protected
50 on both sides with a tin layer), with both iron (Fe) and tin (Sn) are the main constituents.
51 Metals (alloy components as well as impurities) may be released in food from tinplate cans
52 by electrochemical corrosion reactions in aqueous medium through formation of galvanic
53 cells. Such cells are formed when two dissimilar metals are coupled; the more active metal
54 (the anode) dissolves, thus protecting the passive metal (the cathode). Therefore, for tin to be
55 protective it has to be anodic to the steel. The impurities and microscopic faults present on
56 the metal surface may further lead to formation of local cells generating undesirable
57 corrosion currents. Tin coupled to steel may be either the anode or the cathode, depending on
58 the corroding medium. In case of low-pH food products packed in plain tin cans, tin is often
59 anodic to steel and affords complete cathodic protection. The oxidation of tinplate, followed
60 by the release of tin ions into the foodstuff, is known as a “sacrificial anode effect”, a
61 physiochemical mechanism that protects the underlying steel from corrosion. Tin dissolution
62 often passes through three stages (Landau & Mannheim, 1970; Ansari *et al.*, 2019): (1) high
63 rate of tin oxide dissolution that generally occurs between 4 to 15 days after canning
64 (Sherlock *et al.*, 1972); (2) lengthy and slow tin release, with almost constant corrosion rate;
65 (3) a last stage where large areas of steel are exposed, which results in a high rate of tin and
66 iron dissolution - by this time the can has reached the end of its shelf- life (Landau &
67 Mannheim, 1970).

68 Besides Sn and Fe, other trace metals are prone to be release in the food from tinplate cans,
69 particularly chromium (Cr). Passivation treatments using mainly trivalent chromium oxide
70 and chromium metal are classically applied to prevent uncontrolled oxidation of the tin layer

71 (Jorhem & Slorach, 1987). Tin may also be totally replaced by corrosion-resistant chromium
72 layer, mainly in the can lids (Cederberg *et al.*, 2015). Similarly, nickel (Ni) and zinc (Zn) are
73 sometimes intentionally added to enhance cans resistance to rusting and corrosion, while
74 copper (Cu) could be present to provide a hardening advantage (Cederberg *et al.*, 2015).
75 Other metals such as lead (Pb) and cadmium (Cd) are also likely present as impurities
76 (Cederberg *et al.*, 2015). In fact, the old cans soldering technique used tin-lead alloys (which
77 was a great source of dietary lead), soon replaced by lead-free electrowelded side seaming.
78 However, the tin layer itself might still be a source of lead in canned foods since both
79 elements coexist in the ore (Jorhem & Slorach, 1987).

80 Determination of trace metals in canned foods is very important since it gives information
81 about the contamination process and helps in improving canned food quality and safety. High
82 concentrations of essential metals (such as Fe, Ni, Zn and Cu) may still have adverse effects
83 on consumers' health or organoleptic properties of food. There is also health concern related
84 to Sn, with high food levels (i.e. above 200 mg/kg) causing gastrointestinal symptoms and
85 diarrhea (Blunden & Wallace, 2003), as well as Cr since Cr(VI) is highly toxic and Cr (III),
86 considered as essential for humans and the main form found in canned food (Cederberg *et al.*,
87 2015), may be oxidized upon ingestion. Also, Cd and Pb are recognized as neurotoxic
88 compounds even at low concentrations (Obeid *et al.*, 2014).

89 In order to protect the consumers, the Council of Europe have set specific release limits
90 (SRLs) for trace metals prone to be released from food packaging. These SRLs are as follows
91 (per kg of food): 100 mg - Sn, 40 mg - Fe, 0.25 mg - Cr, 4 mg - Cu, 0.14 mg - Ni, 5 mg - Zn,
92 0.01 mg - Pb and 0.005 mg – Cd (Council of Europe, 2013). In addition, the European
93 regulation (Council Directive 1881/2006/EC, 2006) fixed maximum levels (MLs) for Sn (200

94 mg/kg) in canned foods, as well as Pb (0.1-0.2 mg/kg) and Cd (0.05 mg/kg) in fruits
95 including canned fruits.

96 Canned foods face commonly long shelf life, up to 5 years. It is now well admitted that
97 release of metals, due to interactions between foodstuffs and the food contact surface of the
98 cans, will continue throughout the product shelf life. It remains difficult to predict the
99 concentration of each metal at the end of the shelf life since the increase in metal levels in the
100 food may not be linear. In practice, different parameters affect the internal corrosion rate
101 including thermal treatment, tinplate variables (impurities and surface defects), foodstuff
102 characteristics (particularly pH/acidity, and the presence of additives or oxidising reagents),
103 presence of air (oxygen) in the headspace, and storage conditions (time and temperature)
104 (Perring & Basic-Dvorzak, 2002; Reilly, 2002).

105 A lacquer is frequently applied on the inner surface of tinplate cans to prevent corrosion,
106 especially subsequent release of Sn and Fe in canned foods (Dey & Agrawal, 2018). Buculei
107 *et al.* (2012, 2014) showed the importance of the organic protective coating and its properties
108 (e.g. porosity) on the migration phenomenon. Yet, uncoated (or plain) cans are commonly
109 used for fruits since colour changes of fruit (e.g. apricot) pieces have been reported in
110 lacquered cans (Tošković *et al.*, 2015). Since canned fruits are acidic media (pH < 4.5) (Divis
111 *et al.*, 2017), they are expected to offer favoured conditions for trace metals' release due to
112 corrosion (Reilly, 2002; Ansari *et al.*, 2019). In addition, fruits have significant natural
113 variation in, for example, pH and acid type and concentration, dependent on variety, maturity,
114 time/place/conditions of harvest, soil chemistry and agricultural practices; these are difficult
115 for a canner to control and may ultimately impact on the level of trace metals uptake by the
116 product. In this context, the aim of the present study is to investigate the influence of storage
117 time and temperature, can denting, and leaving opened cans in the fridge on the migration of

118 Fe, Sn, Cr, Pb, Cd, Cu, Ni and Zn from uncoated tinplate cans into fruit cocktails, peaches
119 and pears. The migration of metal elements was also compared between different brands of
120 totally uncoated or partially coated (on side seam) tinplate cans of fruit cocktail products.

121 **Materials and Method**

122 *Reagents*

123 All reagents used were of analytical grade. Standard solutions were freshly prepared through
124 dilution of stock solutions with ultrapure water. Fe, Sn, Cd, Pb and Zn standard solutions
125 were prepared from 1000 ± 4 mg/L stock solutions from Fluka Analytical (Buchs,
126 Switzerland), and those of Ni, Cu, and Cr were prepared from 1000 ± 10 mg/L stock
127 solutions from HACH (Dusseldorf, Germany). Microwave digestion was performed with
128 nitric acid (69%; AnalaR, England) and hydrogen peroxide (30-31%; Sigma Aldrich, USA).
129 All glassware was soaked in nitric acid (1%) overnight and then rinsed with ultrapure water.

130 *Sample collection and storage conditions*

131 A total of 69 cans of fruit cocktail, peach halves and pears halves were purchased from the
132 local market of Lebanon. The main properties of the studied samples and the experimental
133 design are detailed in **Table 1**. Note that three cans were considered for each experiment.
134 Fruit cocktail cans were from different brands (A, B and C). Cans of same fruit product had
135 the same production batch number.

136 **Table 1:** Samples properties and storage conditions

	Brand	Purchase time (months)	pH \pm SD†	Fruit size	Can coating	Free space (cm)	Can aspect	Storage temperature ($^{\circ}$ C \pm SD)	Storage time (months)
Fruit cocktail	A	7	4 ± 0.05	Small pieces	Uncoated	0.5	Normal	Refrigerator (5 ± 1) Room temperature (22 ± 4) Oven (40 ± 2)	9, 19, 24 7, 9, 12, 19, 24 9
							Dented	Room temperature (22 ± 4)	9, 19, 24
	B	7	3.49 ± 0.10	Small pieces	Coated on side seam	0	Normal	Refrigerator (5 ± 1) Room temperature (22 ± 4) Oven (40 ± 2)	24 7, 24 12
								Stored opened	Refrigerator (5 ± 1)
C	9	3.83 ± 0.05	Small pieces	Uncoated	0	Normal	Room temperature (22 ± 4)	9, 24	
Peach halves	A	10	3.54 ± 0.04	Fruit halves	Uncoated	0.7	Normal	Room temperature (22 ± 4)	10, 24
Pears halves	A	12	3.71 ± 0.10	Fruit halves	Uncoated	0.5	Normal	Room temperature (22 ± 4)	12, 24

n= 3 cans per experiment; †: SD of pH was determined on 3 cans per fruit product

138

139 After purchase, fruit cocktail samples from brands A and B were divided into three groups
140 that were stored at different temperatures i.e. in refrigerator ($5 \pm 1^\circ\text{C}$), at room temperature
141 ($22 \pm 4^\circ\text{C}$) and in the oven ($40 \pm 2^\circ\text{C}$), since 5°C and 40°C are the temperatures
142 recommended in European regulation for testing migration with food simulants. The
143 remaining fruit products were stored at room temperature. Moreover, another group of fruit
144 cocktail samples from brand A was willingly dented and stored at room temperature. All
145 samples were analyzed at different time intervals between purchase date and until their shelf
146 life (2 years) as indicated in **Table 1**. Finally, the effect of keeping food in their cans in the
147 refrigerator was investigated through opening three cans of fruit cocktail (brand A) and
148 keeping them in the refrigerator (in-home storage conditions) for 10 days.

149 *Sample treatment*

150 The total content (syrup and fruits) of three cans from each sample were homogenized in a
151 stainless steel blender. Three replicates of 2 g from each mixture were accurately weighed
152 into a modified polytetrafluoro-ethylene (PTFE-TFM) microwave bomb vessel. Then 7 mL
153 of nitric acid and 1 mL of hydrogen peroxide were added. The digestion was performed in a
154 high-performance microwave digestion system (Anton Paar, Multiwave 3000, Graz, Austria)
155 according to a program previously described (Kassouf *et al.*, 2013). The final clear digest was
156 then completed to 25 mL with ultrapure water and filtered with 4 μm PTFE filters for
157 subsequent analysis by Atomic Absorption Spectrometry (AAS). During the analysis of some
158 elements, the samples were further diluted to remain within the linearity range of the AAS.
159 Method quantification (MQL) and detection limits (MDL) were determined by analyzing 10
160 method blanks, which were prepared following the previously described analytical method.

161 ***Instrumental conditions***

162 All elements were analyzed by a Thermo Electron Corporation Atomic Absorption
163 Spectrometer with data acquisition carried on Thermo SOLAAR (version 10.11) software.
164 Fe, Sn and Zn were analyzed on a flame atomic absorption spectrometer (FAAS). The
165 analysis of Fe and Zn were respectively performed at $\lambda = 248.3$ and 213.9 nm, with an air–
166 acetylene flame while Sn absorption was analyzed at $\lambda = 286.3$ nm using a nitrous oxide–
167 acetylene flame. Graphite furnace atomic absorption spectrometer (GFAAS) was used with
168 argon as inert gas for determining Pb ($\lambda = 217$ nm), Cd ($\lambda = 228.8$ nm), Cu ($\lambda = 324.8$ nm),
169 Ni ($\lambda = 323$ nm) and Cr ($\lambda = 357.9$ nm). The GFAAS instrument was equipped with a D2
170 lamp for background correction. Calibration stock standards were appropriately diluted to
171 calibrate the spectrometer within the ranges shown in **Table 2**. A buffer solution (0.2% w/v
172 KCl of 1 g/L) was added to both the Sn standard and sample solutions to reduce its ionization
173 in the nitrous oxide–acetylene flame (temperature around 2800°C). For Fe and Zn analysis,
174 strontium releasing agent (1 g/L) was used in order to overcome most common interferences
175 in air-acetylene flame. In the case of GFAAS, matrix modifier (4% v/v mixture of 1 g/kg
176 magnesium nitrate and 1 g/kg of ammonium phosphate solution) was used to trap Cd and Pb
177 during matrix ashing in order to overcome the matrix effect.

178 ***Method accuracy***

179 For validating the used methodology, white cabbage certified reference material (BCR[®]-679,
180 Sigma Aldrich, Geel, Belgium) was analyzed using the same analytical method. This
181 reference material contains all targeted elements, except Pb and Sn. So, the latter two
182 elements were spiked into fruit cocktail samples, in the homogenized mixture prior to
183 microwave digestion, at three concentration levels covering the working ranges of Pb and Sn
184 (**Table 2**).

185 **Statistical analysis**

186 The obtained data was analyzed with the XLStat and Microsoft Excel software (2007).
 187 Testing for significance of mean effects and interactions on all variables was calculated using
 188 ANOVA analysis of variance. Statistical significance was set at $p \leq 0.05$.

189 **Table 2:** Validation data of our analytical method.

Performances of the method					
Metal	Instrument	Linearity Range <i>mg/L</i>	R²	MDL <i>mg/kg</i>	MQL <i>mg/kg</i>
Fe	FAAS	0.5-5	0.9998	0.65	1.7
Sn	FAAS	5-50	0.9998	9.8	25.4
Zn	FAAS	0.2-1.2	0.9997	0.33	1.1
Pb	GFAAS	0.005 – 0.070	0.9976	0.0093	0.0301
Cd	GFAAS	0.000125 – 0.0075	0.9915	0.0017	0.0021
Cu	GFAAS	0.006 – 0.040	0.9910	0.0104	0.0288
Ni	GFAAS	0.005 – 0.050	0.9930	0.0171	0.0610
Cr	GFAAS	0.0009 – 0.0045	0.9930	0.0028	0.0090

Recoveries of trace metals using CRM and spiked samples				
Metal	Validation sample	Expected concentrations <i>mg/kg</i>	Estimated concentrations <i>g/kg</i>	Recoveries <i>%</i>
Fe	CRM (BCR [®] -679)	55.0 ± 2.5	59.7 ± 2.0	108.5 ± 3.6
Cr		0.60 ± 0.10	0.60 ± 0.04	100.0 ± 6.6
Cd		1.66 ± 0.07	1.51 ± 0.05	90.9 ± 3.0
Ni		27.0 ± 0.8	26.7 ± 3.0	98.8 ± 11.1
Cu		2.89 ± 0.12	2.65 ± 0.14	91.7 ± 4.8
Zn		79.7 ± 2.7	74.8 ± 3.3	93.8 ± 4.1
Sn		Spiked samples	25.0	25.3 ± 0.96
	187.5		196.3 ± 6.7	104.7 ± 3.6
	375.0		341.8 ± 9.9	91.2 ± 2.6
Pb	0.050		0.054 ± 0.006	108.0 ± 13.3
	0.100	0.091 ± 0.006	90.8 ± 5.8	
	0.200	0.170 ± 0.015	82.8 ± 7.5	

190

191

192

193 **Results and discussion**

194 *Method performance*

195 Quantification was performed with external calibration using five concentration level. R^2
196 values of linearity were in the range of 0.9910-0.9998 (**Table 2**). MDL and MQL in **Table 2**
197 were calculated as the blank signal, plus 3 and 10 times, respectively, its standard deviation
198 (SD) (Feinberg, 2001). Method recoveries were found satisfactory, ranging from 90 to 110%
199 (**Table 2**).

200 *Metal content in canned fruits*

201 As tin, iron and chromium are by far the main constituents of can's metallic layers, they are
202 more likely to be released into the food. At purchase, the highest concentrations in our
203 canned food samples were thus obtained for these three elements: Sn 28.2-75.7 mg/kg (which
204 remains below its ML value in food), Fe 3.14-8.54 mg/kg and Cr 0.19-0.45 mg/kg. In our
205 previous study (El Moussawi *et al.*, 2019), Sn was not detected in acidic vegetables stored in
206 coated cans: this clearly shows that lacquering with organic coating minimizes tin
207 dissolution, and this suggests that tin found in uncoated canned fruits is mainly released from
208 the can. This is consistent with previous studies: ten times less concentrations of Sn were
209 present in fruits stored in protected cans than in non-protected or partially protected tinplate
210 cans (Rončević *et al.*, 2012; Divis *et al.*, 2017).

211 Our values are in the ranges reported by other authors for canned fruits as indicated in **Table**
212 **3**. In some cases, broad ranges were reported due to different types of cans or brands
213 considered, as well as some discrepancy in storage time and conditions of canned fruits
214 before analysis.

215 **Table 3:** Comparison of the metal levels found in our samples (at purchase) with values reported in tinplate canned fruits^a by other authors.

Canned fruits	Fe <i>mg/kg</i>	Sn <i>mg/kg</i>	Cr <i>mg/kg</i>	Cd <i>µg/kg</i>	Pb <i>µg/kg</i>	Ni <i>mg/kg</i>	Cu <i>mg/kg</i>	Zn <i>mg/kg</i>	References
Peach halves	4.79	28.2	0.19	5.16	< 9.3	0.28	0.29	1.15	This study
Pear halves	4.72	28.6	0.19	5.24	< 9.3	0.34	0.27	1.77	
Fruit cocktails	3.14 – 8.54	36.9 – 75.7	0.20 – 0.45	2.22 – 8.71	< 9.3	0.29 – 0.94	0.25 – 0.35	1.35 – 2.58	
Peach compote		1.69 – 22.37	0.012 – 0.085	8 - 33	3.2 – 9.9				Divis <i>et al.</i> 2017
Pear compote		12.6 – 23.5	0.028 – 0.031	13 - 16	1.8 – 3.7				
Apricot compote		1.63 – 50.33	0.015 – 0.021	9 - 15	1.5 – 7.6				
Pineapple compote		19.2 – 52.3	0.028 – 0.072	14 - 35	1.9 – 3.2				
Mango compote		1.61 – 1.83	0.015 – 0.018	8 - 9	0.8 – 1.1				
Peach, orange, cherry, pineapple		0.071 – 0.14		1.09 - 5.56	470.6 - 910.1				Fathabad <i>et al.</i> 2018
Peaches, pears, apricots		< 0.01 – 150			< 10 – 54				FSANZ 2015
Mango pulp	near 5	54.05 – 64.06							Parkar & Rakesh 2014
Peach halves		28.6 – 82.8							Rončević <i>et al.</i> , 2012
Fruit cocktails		108.6 – 117.3							
Peach halves		57.9							Perring & Basic-Dvorzak 2002
Pear halves		58.9							
Fruit cocktails		73.2							
Pineapples in syrup		113.5							
Pear, peach and apricot halves		44 - 48							Boutakhrit <i>et al.</i> 2011
Fruit cocktail		103							
Mango slices		148							
Pineapple slices		63							

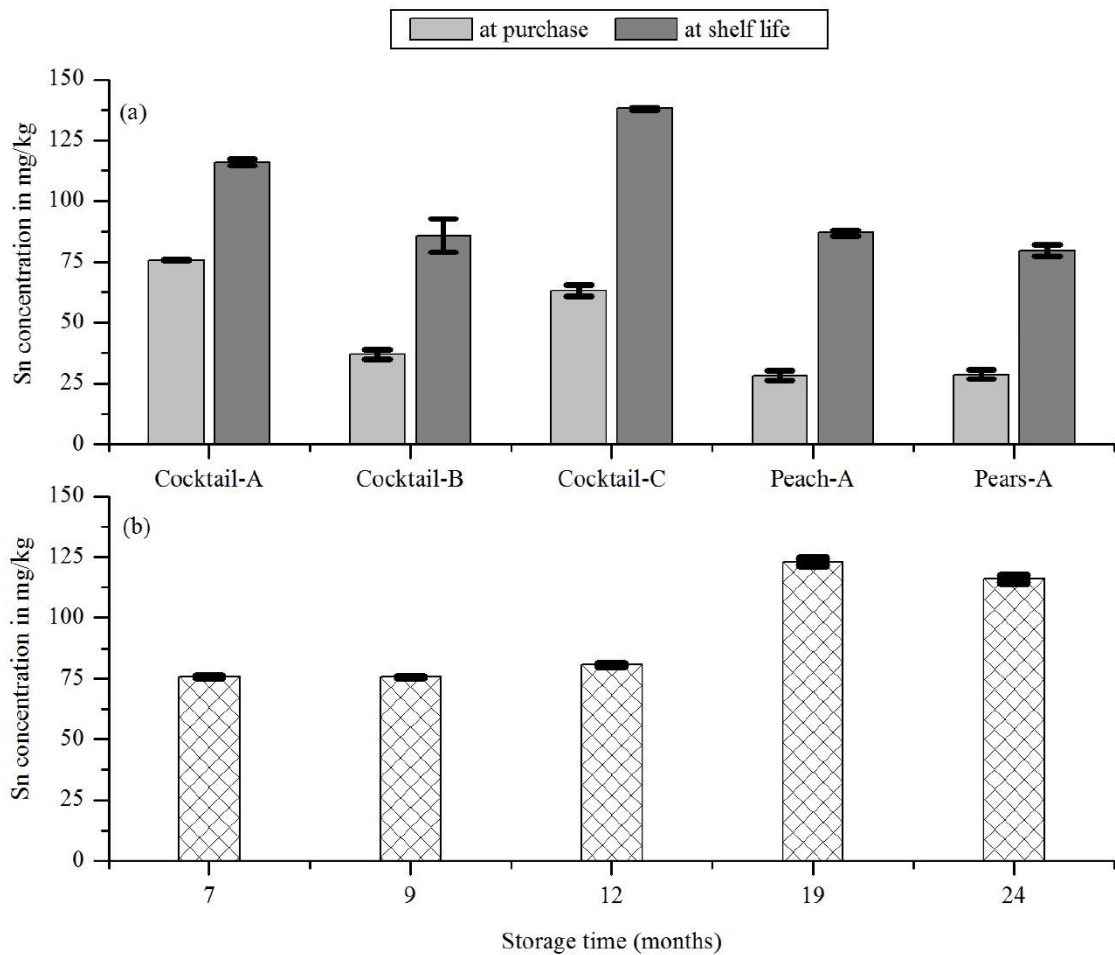
216 ^a fruit juices excluded; grey boxes: element not analysed in the considered reference.

217 Also, our Fe levels are in close range to values reported for mango pulp (Parkar and Rakesh,
218 2014) and canned vegetable in previous Lebanese studies (Nasreddine et al., 2010; Korfali &
219 Hamdan, 2013; El Moussawi *et al.*, 2019). On the other hand, our Cr concentrations are
220 higher by a factor of ten than the Cr levels reported by Diviš *et al.* (2018) in canned fruits;
221 additional data should be required for possible detailed comparison, since for all trace metals
222 broad range of levels are on the whole observed. One explanation lies in the chromium
223 passivation treatment that could have been applied in our tinplate cans, thereby leading to
224 higher levels in the canned fruits.

225 All our samples comply with the ML of 50 µg/kg set for Cd in canned fruits, with levels in
226 the range 2.22 - 8.71 µg/kg. This is in agreement with previous concentrations reported for
227 this metal in canned fruits as shown in **Table 3** (Diviš *et al.*, 2017; Fathabad *et al.*, 2018).
228 Relatively moderate levels of Ni (0.28 - 0.94 mg/kg), Cu (0.25 – 0.35 mg/kg) and Zn (1.15-
229 2.58 mg/kg) were also found in our samples. Interestingly, Pb remained undetected in our
230 samples, being in the same order of values previously reported by Diviš *et al.* (2017). The
231 study from the Food Standards Australian New Zealand (2015) reported Pb levels from
232 undetected to 54 µg/kg in canned peaches and pears (see **Table 3**). Much higher
233 concentrations of Pb were reported in canned fruits purchased in local supermarkets in Iran
234 (Fathabad *et al.*, 2018), possibly due to environmental contamination of the fruits before
235 canning.

236 Whatever the metals considered, similar levels are noted for peach and pear halves; the same
237 trend has been reported in previous studies as indicated in **Table 3**. On the other hand, fruit
238 cocktails exhibit higher levels for the same can brand as illustrated in **Figure 1a**. So, the size
239 of the fruits could have played a role on the release of metal elements; the larger fruit halves

240 possess lower fruit to can contact surface than the smaller pieces of the cocktail, thus limiting
241 metal release from the can and subsequent metal uptake by the fruit pieces.



242

243 *Figure 1: Evolution of Sn between purchase date and shelf life: (a) in canned fruits from*
244 *brands A, B and C; (b) as a function of time in fruit cocktail brand A*

245 Finally, the amount of metal elements measured at purchase was significantly different
246 ($p < 0.05$) between the brands (A, B, C). For example, the lowest levels of all of Sn, Cr, Ni and
247 Cu were detected in fruit cocktails of brand B (**Figure 1a and Table 4**), possibly due to the
248 presence of protective coating on the side seam of these cans. Other elements, like Cr and Ni,
249 were found in the highest levels in brand C canned fruits. Nonetheless, measuring the content

250 of elements at purchase is not sufficient to determine whether the elements are originated
251 from the food or released from the cans, thus it is essential to monitor the evolution of metal
252 elements as a function of storage conditions.

253 *Effect of storage time at room temperature*

254 Upon storage, the migration of metals from the can into its content is not a simple
255 relationship, and migration rate may vary over time (Buculei *et al.* 2014). Thus, no significant
256 relationship was found between the age of the can (from 1 to 3 years) and the tin
257 concentration of canned fruits (Divis *et al.* 2017). Migration is also linked to the
258 electrochemical properties of the metals, so that some initial metals present in the food may
259 be replaced by other metals released from the can.

260 The release of Sn over storage under ambient conditions was significant ($p < 0.05$) in all our
261 samples. According to **Table 4** and **Figure 1a**, Sn levels increased by a minimum value of
262 53% (fruit cocktail / brand A) and up to 208% (peach halves / brand A). In the meantime, the
263 migration of Fe was either very low or insignificant over the studied time interval. These
264 results are consistent with the “sacrificial anode effect” played by the tin layer. Our data are
265 clear indication of the good protection offered by the tin layer in our plain tinned cans,
266 thereby avoiding or limiting steel plate corrosion and Fe release. Considering the reported
267 three-stage anodic tin dissolution (Landau & Mannheim, 1970), the period considered in our
268 study (7 to 24 months) is probably related to the second stage, where tin dissolution is slow
269 and continuous. The slow-down of Sn migration after 6 months was also observed with
270 canned mango pulp: this was suspected to be due to oxygen present in the canned food that
271 favors tin corrosion and Sn release at the beginning of storage, the slow-down being
272 explained as the residual oxygen concentration decreases over time (Parker and Rakesh
273 2014).

274 The migration rates assessed based on our data are in agreement with previous studies related
275 to metals migration from canned fruits as indicated in **Table 5**, with ambient migration rates
276 of around 1 mg/kg/week for Sn and below 0.2 mg/kg/week for Fe. Also, stabilization of Fe
277 levels around 9 months is noted (see **Table 4**), as already reported for other canned foods
278 (Kassouf *et al.*, 2013; Buculei *et al.*, 2014).

279 Again, pear and peach halves show the same trend. For fruit cocktails, some discrepancy is
280 observed with the brand, possibly due to slight variations of canned fruits pH and differences
281 in can material composition (i.e. content of each metals). There is a lack of knowledge in
282 literature on the potential release of metals prone to be present in the alloy or as impurities.
283 As reported for other canned foods in our previous study (El Moussawi *et al.*, 2019), Ni and
284 Zn showed close migration trend to Sn, while Cr, Cd and Cu had a tendency to long-term
285 slow migration. Again, it is interesting to note that most metals' evolution during storage up
286 to shelf life was very similar between canned peach and pear products (e.g. Sn, Cr, Cd and
287 Cu levels increased by about 208%, 42%, 284% and 131% respectively in peaches, and by
288 178%, 37%, 305% and 126% in pears).

289 Overall, all our canned fruits comply with regulation related to Sn (i.e. SRL 100 mg/kg and
290 ML 200 mg/kg) and Pb. On the opposite, most of our samples face Ni migration that exceeds
291 its SRL value of 0.14 mg/kg. There is also concern for Cd release in peaches, pears and fruit
292 cocktails of brand B, with release over the SRL value of 5 µg/kg, but still with levels below
293 the ML of 50 µg/kg.

294 **Table 4:** Evolution of trace metals in canned fruits (stored at room temperature) as a function of storage time

Product	Brand	Time (months)	Fe (mg/kg)	Sn (mg/kg)	Cr (mg/kg)	Cd (µg/kg)	Pb (µg/kg)	Ni (mg/kg)	Cu (mg/kg)	Zn (mg/kg)
Fruit cocktail	A	7	3.14 ± 0.27 ^a	75.7 ± 0.13 ^a	0.26 ± 0.01 ^a	2.22 ± 0.00 ^a	ND	0.46 ± 0.04 ^a	0.27 ± 0.02 ^a	2.58 ± 0.00 ^a
		9	4.63 ± 0.24 ^b	75.6 ± 0.02 ^a	0.33 ± 0.01 ^b	2.22 ± 0.00 ^a	ND	0.62 ± 0.02 ^b	0.30 ± 0.03 ^a	2.87 ± 0.00 ^b
		12	4.20 ± 0.50 ^b	80.7 ± 0.38 ^b	0.27 ± 0.03 ^a	4.41 ± 0.00 ^b	ND	0.70 ± 0.02 ^c	0.27 ± 0.02 ^a	3.24 ± 0.16 ^c
		19	-	123 ± 1.33 ^c	0.38 ± 0.02 ^c	4.21 ± 0.18 ^b	ND	0.87 ± 0.00 ^d	0.38 ± 0.01 ^b	3.68 ± 0.26 ^d
		24	4.59 ± 0.25 ^b	116 ± 1.42 ^d	0.42 ± 0.04 ^c	3.81 ± 0.29 ^b	ND	0.94 ± 0.07 ^d	0.36 ± 0.01 ^b	3.15 ± 0.24 ^c
	% evolution (7-24 months)		46.2 %	53.2 %	61.5 %	71.6 %	-	104.3 %	33.3 %	22.1 %
	B	7	8.54 ± 0.23 ^a	36.9 ± 2.10 ^a	0.20 ± 0.02 ^a	8.71 ± 0.20 ^a	ND	0.29 ± 0.02 ^a	0.25 ± 0.03 ^a	2.19 ± 0.26 ^a
		24	8.41 ± 0.18 ^a	85.7 ± 6.90 ^b	0.24 ± 0.03 ^a	24.07 ± 0.96 ^b	ND	0.40 ± 0.07 ^b	0.82 ± 0.05 ^b	3.19 ± 0.31 ^b
		% evolution (7-24 months)		Insignificant	132.2 %	Insignificant	176.3 %	-	37.9 %	228.0 %
	C	9	6.86 ± 0.69 ^a	63.2 ± 2.30 ^a	0.45 ± 0.03 ^a	7.45 ± 0.70 ^a	ND	0.94 ± 0.11 ^a	0.35 ± 0.01 ^a	1.35 ± 0.09 ^a
24		6.08 ± 0.52 ^a	138 ± 9.40 ^b	0.43 ± 0.01 ^a	9.73 ± 0.32 ^b	ND	1.24 ± 0.10 ^b	0.65 ± 0.06 ^b	2.74 ± 0.23 ^b	
% evolution (9-24 months)		Insignificant	118.3 %	Insignificant	30.6 %	-	31.9 %	85.7 %	102.9 %	
Peach halves	A	10	4.79 ± 0.49 ^a	28.2 ± 2.10 ^a	0.19 ± 0.00 ^a	5.16 ± 0.40 ^a	ND	0.28 ± 0.00 ^a	0.29 ± 0.03 ^a	1.15 ± 0.17 ^a
		24	6.55 ± 0.26 ^b	86.9 ± 1.20 ^b	0.27 ± 0.01 ^b	19.81 ± 2.01 ^b	ND	0.48 ± 0.02 ^b	0.67 ± 0.04 ^b	1.36 ± 0.02 ^a
	% evolution (10-24 months)		36.7 %	208.1 %	42.1 %	284 %	-	71.4 %	131 %	Insignificant
Pears halves	A	12	4.72 ± 0.60 ^a	28.6 ± 1.80 ^a	0.19 ± 0.00 ^a	5.24 ± 0.09 ^a	ND	0.34 ± 0.01 ^a	0.27 ± 0.02 ^a	1.77 ± 0.05 ^a
		24	5.44 ± 0.46 ^a	79.6 ± 2.40 ^b	0.26 ± 0.01 ^b	21.25 ± 1.65 ^b	ND	0.43 ± 0.03 ^b	0.61 ± 0.03 ^b	1.87 ± 0.04 ^a
	% evolution (12-24 months)		Insignificant	178.3 %	36.8 %	305 %	-	26.5 %	125.9 %	Insignificant

295 Superscripts ^{a, b, c, d} correspond to significantly different concentrations of metals (p<0.05), whereas concentrations showing same letter are close

296

297 **Table 5:** Comparison of the migration rate estimated in our samples with values from other reported studies.

Canned food and storage conditions after purchase	Fe mg/kg/week	Sn mg/kg/week	Cr mg/kg/week	Cd µg/kg/week	Ni mg/kg/week	Cu mg/kg/week	Zn mg/kg/week	References
Peach halves – brand A								This study
22°C – 14 months	0.0314	1.048	0.0014	0.262	0.0036	0.0068	0.0037	
Pear halves – brand A								This study
22°C – 12 months	0.015	1.063	0.0015	0.334	0.0019	0.0071	0.0021	
Fruit cocktails – brand A								This study
22°C – 2 months	0.186	-0.0125	0.0088	0	0.0020	0.0037	0.0362	
22°C – 17 months	0.0213	0.593	0.0023	0.0234	0.0071	0.0013	0.0084	
40°C – 2 months	15.48	33.66	0.0363	0.260	0.035	0.0225	0.240	
Fruit cocktails – brand B								This study
22°C – 17 months	-0.0019	0.718	0.00059	0.226	0.0016	0.0084	0.0147	
40°C – 5 months	49.77	25.05	0.0095	0.621	0.005	0.0250	0.0240	
Fruit cocktails – brand C								This study
22°C – 15 months	-0.013	1.247	-0.00033	0.038	0.005	0.005	0.0232	
Fruit cocktails – brand A								This study
22°C – 2 months – dented cans	0.302	4.188	0.0138	0.261	0.005	0.0188	0.070	
22°C – 12 months – dented cans		1.023	0.0021	0.0475	0.0127	0.0048	0.0210	
22°C – 17 months – dented cans	0.0235	0.560	0.0026	0.0249	0.0066	0.0022	0.0193	
Fruit cocktails – opened cans								This study
5°C – 10 days	73.40	103.11	-0.0028	0	0.0035	0.0119	0	
Mango pulp								Parker & Rakesh 2014
28°C – 3 months	near 0.02	1.578						
28°C – 12 months	near 0.02	1.421						
38°C – 6 months	near 0.54	15.48						
38°C – 12 months	near 36	6.22						
48°C – 6 months	near 100	20.96						
Tomato paste (different brands)								Gordon <i>et al.</i> 2015
<=4°C – 6 weeks	0.0429 - 2.246	<0.0001 - 0.0137						
28°C – 6 weeks	0.683 - 9.691	0.0025 - 0.163						

32°C, humid – 6 weeks	3.165 - 18.138	0.0902 - 0.257	
Tomatoes			Buculei <i>et al.</i> 2012
25°C – 3 years	near 0.06	0.6 - 0.14	

298 *Values in grey and italic characters: insignificant migration. Striking values are shown in bold characters.*

299 *Effect of storage temperature*

300 It has been reported that the corrosion process obeys the Arrhenius type reaction, so that
301 corrosion rate of tinfoil in fruit juices was reported to increase with temperature (from 10 to
302 55°C) (Dey & Agrawal, 2017). In Lebanon and other countries, can storage under elevated
303 temperatures may occur, especially when cans are left to sun exposure. So, 40°C was tested
304 here to simulate storage in hot areas. Hence, Fe contents in various canned drinks was found
305 to increase upon sunlight exposure of the cans (Rahayu & Asmorowati, 2019). On the
306 opposite, a previous study reported no significant changes in Sn levels for canned tomato
307 paste stored in the fridge (4°C or below) over 6 weeks (Gordon *et al.*, 2015).

308 Surprisingly, at high temperature, our fruit cans were blown after few months (2 months for
309 brand A and 5 months for brand B) due to important corrosion. In fact, under high storage
310 temperature, the tin layer is more likely to be released, leaving unprotected steel to corrode
311 very rapidly with vigorous evolution of hydrogen (Blunden & Wallace, 2003). Consequently,
312 Fe and Sn levels drastically increased in these samples (up to near 120 times as indicated in
313 **Supplementary Table 1**), exceeding the regulated values for both elements (SRL of 40
314 mg/kg for Fe; SRL of 100 mg/kg and ML of 200 mg/kg for Sn respectively). This evolution
315 of Fe and Sn is in agreement with two other studies also made on plain tin cans of fruits
316 (Calloway & McMullen, 1966; Parkar & Rakesh, 2014), where their content increased by up
317 to 12 fold when the storage temperature increased from 37 to 48°C.

318 The significant impact of 40°C was also noticed on the remaining metals, but to less extend
319 than Fe and Sn (see **Table 5** and **Supplementary Table 1**). In particular, Pb was not detected
320 in fruit cocktail of brand A even at high temperature, but it reached 57 µg/kg in brand B at
321 40°C where it exceeded its SRL value of 10 µg/kg. This result reflects the importance of the
322 purity of metal substrates used in the studied cans.

323 Low storage temperature (5°C) was significant on slowing down the migration of most trace
324 metals at earlier storage time (between 7 and 9 months in brand A). However, in most cases
325 close concentrations were reached at 24 months between cans stored at 5 and 22°C (see
326 **Supplementary Table 1**).

327 *Effect of can denting*

328 Good practices recommend to handle canned foods with caution in order to avoid damaging
329 the cans, since it is now well-known that can denting leads to deterioration of the different
330 layers in the tinplate, with subsequent enhanced corrosion and release of trace metals such as
331 Fe and Pb (Kassouf *et al.*, 2013). As expected, we have observed higher levels of Fe, Sn and
332 Cd (extra levels of 20, 44 and 94%, respectively) in dented cans than in the same undented
333 cans (**Supplementary Table 2**). Yet, surprisingly, at shelf life, equal concentrations were
334 reached for these metals in both types of cans (for example Sn was present at 114 mg/kg in
335 dented cans and 116 mg/kg in normal cans at 24 months). Thus, upon denting, the
336 equilibrium of Fe, Sn and Cd release is reached faster as shown by the estimated migration
337 rates (see **Table 5**). On the other hand, different behaviour was observed for Cu and Zn: still
338 faster release in dented cans at the beginning of storage, but significant higher levels (about
339 20% higher) in dented cans at shelf life. Finally, the content of Cr and Ni was not affected by
340 the denting.

341 *Effect of leaving open cans in the fridge*

342 On the package label there are some instructions for use of an open can in such a way as to be
343 consumed in a maximum period of three days. This period of time is considered as crucial in
344 order to avoid the development of mold, without any consideration on the possible migration of
345 metals from the package material. Yet, previous studies showed strong correlation between the

346 storage time and the content of several metals in the open cans. In particular, storing food in
347 open unlacquered cans led to substantial increases in the tin levels in the food (Perring &
348 Basic-Dvorzak, 2002). This is due to the increased concentration of oxygen upon opening that
349 accelerates corrosion of food cans (Parlar & Rakesh, 2014; Raptopoulou *et al.* 2014, 2018).
350 Recent results suggest that open canned foods should be consumed within 24 hours due to
351 metals migration (Petropoulos *et al.*, 2018); 6 hours after the opening was considered as the
352 crucial time point for food degradation. Alternatively, the can contents should be placed in
353 another container for longer storage.

354 When we kept our open cans for 10 days in the fridge, the tin layer sloughed off and tin
355 content increased by 3 times to reach 223 mg/kg, exceeding its SRL of 100 mg/kg as well as
356 its ML of 200 mg/kg (**Supplementary Table 3**). The steel layer was then attacked and Fe
357 increased by 35 times to reach 108 mg/kg, where about 105 mg/kg of Fe were released within
358 10 days. Copper release was also accelerated in the opened cans (see **Table 5**). Surprisingly,
359 Cr showed a slight significant decrease after opening the cans (15 %), thereby indicating that
360 Cr may only be present in the lids.

361 **Conclusion**

362 Fruits cans are considered at risk of metals migration due to the use of unlacquered tinplate
363 cans as the packaging material to protect fruit quality (such as colour) and their low pH (<
364 4.5) that favours corrosion. Our study shows that fruit cans deserve particular attention and
365 caution during handling and storage, not only in the canner industry and the points of sale,
366 but also at consumer's home. The absence of protective lacquer certainly leads to high release
367 of Sn that showed slow and continuous dissolution as a function of storage time. The tin layer
368 was found effective in preventing steel corrosion and further Fe release in the food. However,
369 corrosion is accelerated under elevated temperature storage (40°C), leading to important

370 release of Sn, Fe and other metal alloys, even exceeding the regulated limits. Similar results
371 are obtained with open cans stored in the fridge for a few days, due to fast oxidation of tin
372 layer; consequently, consumers should be advised against storing food in open tinplate cans.
373 Also, cans with defects (like dented cans) are more prone to corrosion, and higher migration
374 rates were clearly observed for several metals in that case. Finally, the quality and integrity of
375 metal alloy used by the canner industry should be carefully controlled since they affect the
376 quantity of metals released. As an illustration, upon storage for months under ambient
377 temperature, Ni and Cd exceeded their recommended SRL in 50% of our canned fruit
378 samples while Pb remained undetected.

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510

511 **Supplementary Table 1:** Evolution of trace metals in fruit cocktail (brands A and B) as a function of storage temperature

Brand	Storage time (months)	Storage Temp. (°C)	Fe (mg/kg)	Sn (mg/kg)	Cr (mg/kg)	Cd (µg/kg)	Pb (µg/kg)	Ni (mg/kg)	Cu (mg/kg)	Zn (mg/kg)	
A	7	22	3.14 ± 0.27	75.7 ± 0.1	0.26 ± 0.01	2.22 ± 0.00	ND	0.46 ± 0.04	0.27 ± 0.02	2.58 ± 0.00	
	9	5	-	67.6 ± 0.0	0.20 ± 0.01	2.22 ± 0.00	ND	0.38 ± 0.02	0.31 ± 0.00	2.49 ± 0.17	
		22	4.63 ± 0.24	75.6 ± 0.0	0.33 ± 0.01	2.22 ± 0.00	ND	0.62 ± 0.02	0.30 ± 0.03	2.87 ± 0.00	
		40	127 ± 3.5	345 ± 27	0.55 ± 0.02	4.3 ± 0.00	ND	0.74 ± 0.00	0.45 ± 0.03	4.50 ± 0.25	
	19	5	5.50 ± 0.27	106 ± 3	0.39 ± 0.00	3.50 ± 0.60	ND	0.81 ± 0.06	0.40 ± 0.00	3.11 ± 0.02	
		22	6.06 ± 0.72	123 ± 1	0.38 ± 0.01	4.21 ± 0.18	ND	0.87 ± 0.00	0.38 ± 0.01	3.68 ± 0.26	
		40	Not analyzed†								
	24	5	4.96 ± 0.60	107 ± 10	0.42 ± 0.03	2.53 ± 0.09	ND	0.94 ± 0.03	0.35 ± 0.01	2.83 ± 0.01	
		22	4.59 ± 0.25	116 ± 2	0.42 ± 0.04	3.81 ± 0.29	ND	0.94 ± 0.07	0.36 ± 0.01	3.15 ± 0.24	
		40	Not analyzed†								
	B	7	22	8.54 ± 0.23	36.9 ± 2.1	0.20 ± 0.02	8.71 ± 0.20	ND	0.29 ± 0.02	0.25 ± 0.03	2.19 ± 0.26
		12	40	1004 ± 35	538 ± 42	0.39 ± 0.03	21.12 ± 1.88	57.05 ± 1.56	0.39 ± 0.03	0.75 ± 0.04	2.67 ± 0.21
24		5	8.53 ± 0.31	68.9 ± 4.3	0.25 ± 0.02	21.03 ± 0.41	ND	0.27 ± 0.03	0.76 ± 0.01	3.15 ± 0.12	
		22	8.41 ± 0.18	85.7 ± 6.9	0.24 ± 0.03	24.11 ± 0.90	ND	0.40 ± 0.07	0.82 ± 0.05	3.19 ± 0.31	
		40	Not analyzed†								

512 † The cans were blown and could not be analyzed

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514 **Supplementary Table 2: Effect of can denting on the migration of target metals**

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Element	Time (months)	Normal	Dented
Fe (mg/kg)	9	4.63 ± 0.24	5.55 ± 0.02
	24	4.59 ± 0.25	4.74 ± 0.11
Sn (mg/kg)	9	75.6 ± 0.0	109.2 ± 2.7
	19	123 ± 1	124.8 ± 4.0
	24	116 ± 2	113.8 ± 1.0
Cd (µg/kg)	9	2.22 ± 0.00	4.31 ± 0.00
	19	4.21 ± 0.18	4.50 ± 0.14
	24	3.81 ± 0.29	3.91 ± 0.07
Pb (µg/kg)	9	ND	ND
	19	ND	ND
	24	ND	ND
Cr (mg/kg)	9	0.33 ± 0.01	0.37 ± 0.01
	19	0.38 ± 0.02	0.36 ± 0.03
	24	0.42 ± 0.04	0.44 ± 0.01
Ni (mg/kg)	9	0.62 ± 0.02	0.50 ± 0.01
	19	0.87 ± 0.00	1.07 ± 0.05
	24	0.94 ± 0.07	0.91 ± 0.04
Cu (mg/kg)	9	0.30 ± 0.03	0.42 ± 0.04
	19	0.38 ± 0.01	0.50 ± 0.00
	24	0.36 ± 0.01	0.42 ± 0.01
Zn (mg/kg)	9	2.87 ± 0.00	3.14 ± 0.16
	19	3.68 ± 0.26	3.59 ± 0.33
	24	3.15 ± 0.24	3.89 ± 0.19

n= 3 replicates per experiment

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546 **Supplementary Table 3: Effect of leaving opened fruit cocktail cans for 10 days in**
547 refrigerator on the migration of target metals

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Element	Before opening	After opening	p-value
Fe (mg/kg)	3.14 ± 0.27	108 ± 2.5	2.31E-07*
Sn (mg/kg)	75.7 ± 0.13	223 ± 4.7	6.94E-07*
Cr (mg/kg)	0.26 ± 0.01	0.22 ± 0.00	0.0020*
Cd (µg/kg)	2.22 ± 0.00	2.22 ± 0.00	0.327
Ni (mg/kg)	0.46 ± 0.04	0.51 ± 0.01	0.0925
Cu (mg/kg)	0.27 ± 0.02	0.44 ± 0.04	0.0037*
Zn (mg/kg)	2.58 ± 0.00	2.58 ± 0.00	0.608

n= 3 replicates per experiment

*: significantly different concentrations of metals (p<0.05)

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