



Parameters influencing the migration of trace metals in uncoated fruit cans

Sara Nouredine El Moussawi, Valérie Camel, Mathieu Cladière, Nada Lebbos, Hanna Chébib, Rosette Ouaini

► To cite this version:

Sara Nouredine El Moussawi, Valérie Camel, Mathieu Cladière, Nada Lebbos, Hanna Chébib, et al.. Parameters influencing the migration of trace metals in uncoated fruit cans. *Journal of Food Processing and Preservation*, 2020, 44 (9), pp.e14653. 10.1111/jfpp.14653 . hal-03164286

HAL Id: hal-03164286

<https://hal.science/hal-03164286>

Submitted on 9 May 2022

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Parameters influencing the migration of trace metals in uncoated fruit cans

Running title: Migration of metals in uncoated fruit cans

Sara Nouredine El Moussawi^{a,b}, Valérie Camel^a, Mathieu Cladière^a, Nada Lebbos^c, Hanna Chébib^b and Rosette Ouaini^{b*}

^aUMR Ingénierie Procédés Aliments, AgroParisTech, Inra, Université Paris-Saclay, Massy, 91300, France

^bER004 Lebanese Food Packaging, Faculty of Sciences II, Lebanese University, Fanar, 90656, Lebanon

^cLebanese Agricultural Research Institute, Fanar, Lebanon

* Corresponding author: rouaini@ul.edu.lb

Abstract

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

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

Practical applications

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

Introduction

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

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

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

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

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

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

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

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

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

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

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

Materials and Method

Reagents

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

Sample collection and storage conditions

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

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

	Brand	Purchase time (months)	pH ± SD†	Fruit size	Can coating	Free space (cm)	Can aspect	Storage temperature (°C± 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
							Stored opened	Refrigerator (5 ± 1)	1/3 (i.e. 10 days)
	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
	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

137

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.

Instrumental conditions

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

Method accuracy

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

Statistical analysis

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

Table 2: Validation data of our analytical method.

Performances of the method					
Metal	Instrument	Linearity Range <i>mg/L</i>	R ²	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 %
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	101.2 ± 3.8
		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

Results and discussion

Method performance

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

Metal content in canned fruits

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

Our values are in the ranges reported by other authors for canned fruits as indicated in **Table 3**. In some cases, broad ranges were reported due to different types of cans or brands considered, as well as some discrepancy in storage time and conditions of canned fruits 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							
Pear halves		58.9							Perring & Basic-Dvorzak 2002
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 Divis *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

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

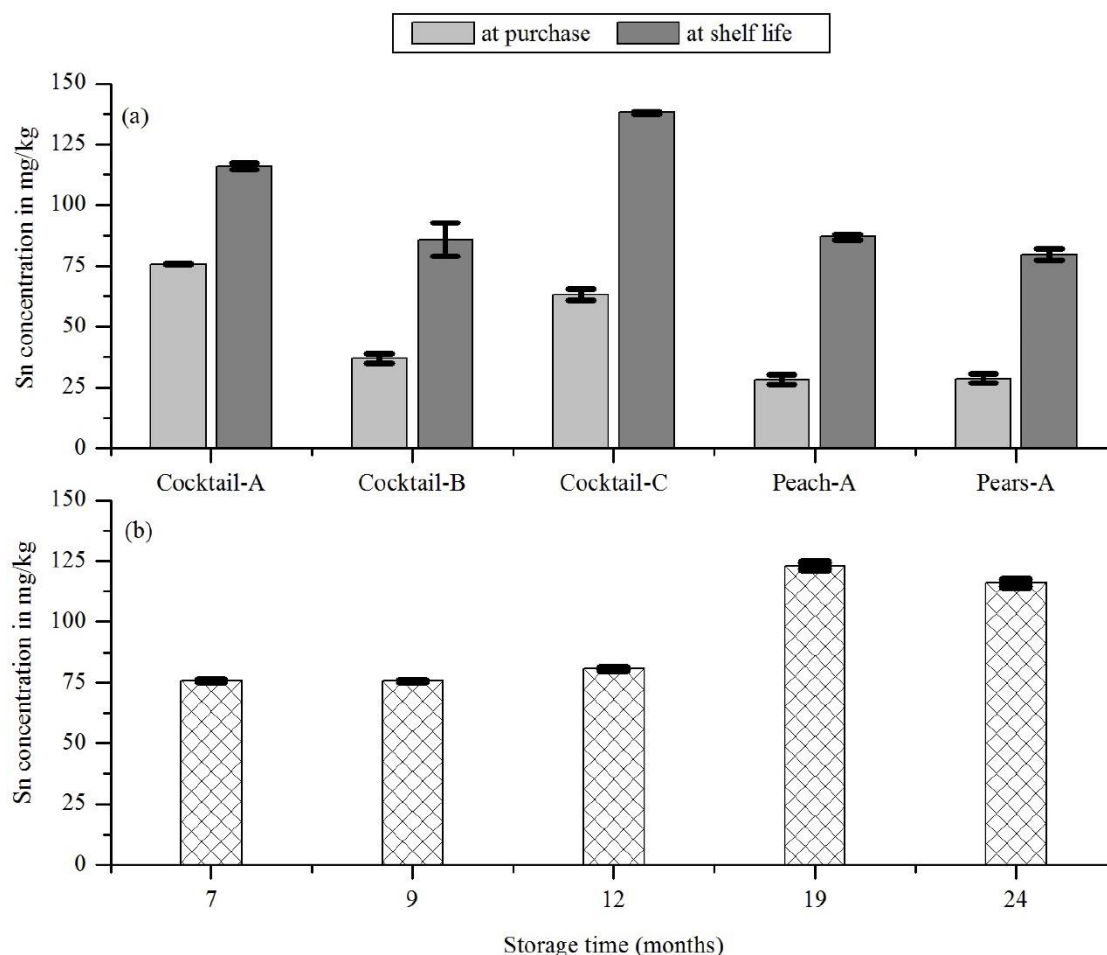


Figure 1: Evolution of Sn between purchase date and shelf life: (a) in canned fruits from brands A, B and C; (b) as a function of time in fruit cocktail brand A

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

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

Effect of storage time at room temperature

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

The release of Sn over storage under ambient conditions was significant ($p < 0.05$) in all our samples. According to **Table 4** and **Figure 1a**, Sn levels increased by a minimum value of 53% (fruit cocktail / brand A) and up to 208% (peach halves / brand A). In the meantime, the migration of Fe was either very low or insignificant over the studied time interval. These results are consistent with the “sacrificial anode effect” played by the tin layer. Our data are clear indication of the good protection offered by the tin layer in our plain tinned cans, thereby avoiding or limiting steel plate corrosion and Fe release. Considering the reported three-stage anodic tin dissolution (Landau & Mannheim, 1970), the period considered in our study (7 to 24 months) is probably related to the second stage, where tin dissolution is slow and continuous. The slow-down of Sn migration after 6 months was also observed with canned mango pulp: this was suspected to be due to oxygen present in the canned food that favors tin corrosion and Sn release at the beginning of storage, the slow-down being explained as the residual oxygen concentration decreases over time (Parkar and Rakesh 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 %	45.6 %
	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 22°C – 14 months	0.0314	1.048	0.0014	0.262	0.0036	0.0068	0.0037	This study
Pear halves – brand A 22°C – 12 months	0.015	1.063	0.0015	0.334	0.0019	0.0071	0.0021	This study
Fruit cocktails – brand A 22°C – 2 months	0.186	-0.0125	0.0088	0	0.0020	0.0037	0.0362	This study
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 22°C – 17 months	-0.0019	0.718	0.00059	0.226	0.0016	0.0084	0.0147	This study
40°C – 5 months	49.77	25.05	0.0095	0.621	0.005	0.0250	0.0240	
Fruit cocktails – brand C 22°C – 15 months	-0.013	1.247	-0.00033	0.038	0.005	0.005	0.0232	This study
Fruit cocktails – brand A 22°C – 2 months – dented cans	0.302	4.188	0.0138	0.261	0.005	0.0188	0.070	This study
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 5°C – 10 days	73.40	103.11	-0.0028	0	0.0035	0.0119	0	This study
Mango pulp 28°C – 3 months	near 0.02	1.578						Parkar & Rakesh 2014
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) <=4°C – 6 weeks	0.0429 - 2.246	<0.0001 - 0.0137						Gordon <i>et al.</i> 2015
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 tinplate 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.

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

Effect of can denting

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

Effect of leaving open cans in the fridge

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

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

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

Conclusion

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

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

Acknowledgment

Sara Noureddine ElMoussawi would like to express her gratitude to the Doctoral School of Science and Technology (EDST) of the Lebanese University for providing her with a scholarship.

References

- Aasheim, E.T., Sharp S.J., Appleby P.N., Shipley M.J., Lentjes M.A.H., Khaw K-T., et al. (2015) Tinned fruit consumption and mortality in three prospective cohorts. *PLoS ONE*, **10**(2), e0117796. <https://doi:10.1371/journal.pone.0117796>.
- Abdelrahman, N.A. (2015). Tin-plate corrosion in canned foods. *Journal of Global Biosciences*, **4**(7), 2966–2971.
- Ansari, F.A., Siddiqui, Y.S. & Quraishi, M.A. (2019). Corrosion of tin can and its inhibition: A review. *International Journal of Corrosion and Scale Inhibition*, **8**(4), 816–834.

391 Anwar, A. Mahmood, T., Khan, M.Z., Kiswar, F., Perveen, R. & Ikram, S. (2014). Heavy
 392 Metals in Fruit Juices in Different Packing Material. *FUUAST Journal of Biology*, **4**, 191–
 393 194.

394 Arvanitoyannis, I.S. & Kotsanopoulos, K.V. (2014). Migration phenomenon in food
 395 packaging. Food–package interactions, mechanisms, types of migrants, testing and relative
 396 legislation—A review. *Food and Bioprocess Technology*, **7**, 21–36.
 397 <https://doi:10.1007/s11947-013-1106-8>.

398 Blunden, S. & Wallace, T. (2003). Tin in canned food: a review and understanding of
 399 occurrence and effect. *Food and Chemical Toxicology*, **41**, 1651–1662.
 400 [https://doi:10.1016/S0278-6915\(03\)00217-5](https://doi:10.1016/S0278-6915(03)00217-5).

401 Boutakhrit, K., Crisci, M., Bolle, F. & Van Loco, J. (2011) Comparison of four analytical
 402 techniques based on atomic spectrometry for the determination of total tin in canned
 403 foodstuffs, *Food Additives and Contaminants*, **28**(2), 173-179.
 404 <https://doi:10.1080/19440049.2010.544679>.

405 Buculei, A. Gutt, G., Sonia, A., Adriana, D. & Constantinescu, G. (2012). Study regarding
 406 the tin and iron migration from metallic cans into foodstuff during storage. *Journal of*
 407 *Agroalimentary Processess and Technologies*, **18**, 299–303.

408 Buculei, A. Amariei, S., Oroian, M., Gutt, G., Gaceu, L., & Birca, A. (2014). Metals
 409 migration between product and metallic package in canned meat. *LWT - Food Science and*
 410 *Technology*, **58**, 364–374. <https://doi:10.1016/j.lwt.2013.06.003>.

411 Calloway, D. H. & McMullen, J. J. (1966). Fecal excretion of iron and tin by men fed stored
 412 canned foods. *The American Journal of Clinical Nutrition*, **18**, 1–6.

413 Cederberg, D.L., Christiansen, M., Ekroth, S., Engman, J., Fabech, B., Guðjónsdóttir, K.,
 414 Håland, J.T., Jónsdóttir, I., Kostaomo, P., Legind, C. and Mikkelsen, B. (2015). *Food*

- contact materials – metals and alloys. Nordic guidance for authorities, industry and trade. Copenhagen: Nordic Council of Ministers, 24-47.
- Council of Europe (2002). *Council of Europe's policy statements concerning materials and articles intended to come into contact with foodstuffs. Technical document on metals and alloys used as food contact materials (13.02.2002)*.
- Council of Europe (2013). *Metals and Alloys Used in Food Contact Materials and Articles: A Practical Guide for Manufacturers and Regulators*. 1st ed. European Directorate for the Quality of Medicines and HealthCare, Strasbourg: pp. 31–165.
- Dey S. & Agrawal M.K. (2017). Investigation of corrosion behavior of tinplate in fruit juice. *International Journal of Engineering & Technology*, **9**(3S), 234–242. <https://doi:10.21817/ijet/2017/v9i3/170903S036>.
- Dey S. & Agrawal M.K. (2018). Evaluation of lacquered tinplate corrosion in canned food through characterization by using SEM & EDS technique. *International Journal of Engineering & Technology*, **7**(4.5), 341–346.
- Diviš, P., Šťávková, E., Pořízka, J., & Drábíková, J. (2017) Determination of tin, chromium, cadmium and lead in canned fruits from the Czech market, *Potravinarstvo Slovak Journal of Food Sciences*, 11(1), 564–570. <https://doi:10.5219/749>.
- El Moussawi, S. N., Ouaini, R., Matta, J., Chébib, H., Cladière, M., & Camel, V. (2019). Simultaneous migration of bisphenol compounds and trace metals in canned vegetable food. *Food Chemistry*, **288**, 228-238.
- European Commission (2006). Commission Regulation (EC) No 1881/2006 of 19 December 2006. Setting maximum levels for certain contaminants in foodstuffs. *Official Journal of the European Union*, 5–24.
- Fathabad, A.E., Shariatifar, N., Moazzen, M., Nazmara, S., Fakhri, Y., Alimohammadi, M., Azari, A. & Khaneghah, A.M. (2018). Determination of heavy metal content of processed

fruit products from Tehran's market using ICP- OES: A risk assessment study. *Food and Chemical Toxicology*. **115**, 436–446. <https://doi:10.1016/j.fct.2018.03.044>.

Feinberg, M. (2001). *L'assurance qualité dans les laboratoires agroalimentaires et pharmaceutiques*. 2nd ed. Paris: Tech.& Doc./Lavoisier, 117–142.

Food Standards Australian New Zealand (2015) FSANZ analytical survey of arsenic, lead and tin in shelf-stable peach, pear and apricot products. <https://www.foodstandards.gov.au/publications/Documents/METALS%20IN%20FRUITS%20-%20FINAL.pdf>

Gordon, A., Yahaya, B., Ayittey, K., Adjei-Mensah, R. (2015). Migration of iron and tin from tin plated coated cans into tomato paste. *International Journal of Applied Research*, **1**(13), 90–94.

Jorhem, L., & Slorach, S. (1987) Lead, chromium, tin, iron and cadmium in foods in welded cans. *Food Additives & Contaminants*, **4**(3), 309-316.

Kassouf, A. Chebib H., Lebbos N. & Ouaini R. (2013). Migration of iron, lead, cadmium and tin from tinsplate-coated cans into chickpeas. *Food additives & contaminants. Part A*, **30**, 1987–1992. <https://doi:10.1080/19440049.2013.832399>.

Korfali, S. I. & Hamdan, W. A. (2013). Essential and Toxic Metals in Lebanese Marketed Canned Food: Impact of Metal Cans. *Journal of Food Research*, **2**, 19–30. <https://doi:10.5539/jfr.v2n1p19>.

Landau, M. & Mannheim, C.H. (1970). Evaluation of electrolytic tinsplates for juice containers, *International Journal Food Science and Technology*, **5**(4), 417-421.

Massadeh, A. M. & Al-massaedh, A. A. T. (2017). Determination of heavy metals in canned fruits and vegetables sold in Jordan market. *Environmental Science and Pollution Research*, **25**, 1914–1920. <https://doi:10.1007/s11356-017-0611-0>.

464 Millour, S., Noël, L., Chekri, R., Vastel, C., Kadar, A., Sirot, V., Leblanc, J-C. & Guérin, T.
 465 (2012). Strontium, silver, tin, iron, tellurium, gallium, germanium, barium and vanadium
 466 levels in foodstuffs from the Second French Total Diet Study. *Journal of Food*
 467 *Composition and Analysis*, **25**, 108-129. <https://doi:10.1016/j.jfca.2011.10.004>.
 468 Nasreddine, L., Nashalian, O., Naja, F., Itani, L., Parent-Massin, D., Nabhani-Zeidan, M., &
 469 Hwalla, N. (2010). Dietary exposure to essential and toxic trace elements from a Total diet
 470 study in an adult Lebanese urban population. *Food and Chemical Toxicology*, **48**, 1262–
 471 1269. <https://doi:10.1016/j.fct.2010.02.020>.
 472 Obeid, P. J. Obeid, P. J., Saliba, C., Younis, M., Aouad, S., & El-Nakat, J. (2014).
 473 Determination of levels of lead and cadmium contamination in meat products sold in
 474 northern lebanese markets. *International Journal of Safety and Security Engineering*, **4**,
 475 329–344. <https://doi:10.2495/SAFE-V4-N4-329-344>.
 476 Parkar, J. and Rakesh, M. (2014). Leaching of elements from packaging material into canned
 477 foods marketed in India. *Food Control*, **40**, 177–184. <https://doi:10.1016/j.foodcont.2013.11.042>.
 478
 479 Perring, L. & Basic-Dvorzak, M. (2002). Determination of total tin in canned food using
 480 inductively coupled plasma atomic emission spectroscopy. *Analytical and Bioanalytical*
 481 *Chemistry*, **374**, 235–243. <https://doi:10.1007/s00216-002-1420-x>.
 482 Petropoulos, G., Raptopoulou, K. G., Pasias, I. N., Thomaidis, N. S., & Proestos, C. (2018).
 483 Chemometric determination of the shelf life of opened cans using the migration of specific
 484 metals as quality indicators. *Food Chemistry*, **267**, 313–318.
 485 <https://doi.org/10.1016/j.foodchem.2017.06.041>
 486 Rahayu, E.F. & Asmorowati, D.S. (2019). Review of metal corrosion on food cans. *Journal*
 487 *of Physics: Conference Series*, **1321**, 022037. [https://doi:10.1088/1742-](https://doi:10.1088/1742-6596/1321/2/022037)
 488 [6596/1321/2/022037](https://doi:10.1088/1742-6596/1321/2/022037).

- Raptopoulou, K. G., Pasias, I. N., Thomaidis, N. S., & Proestos, C. (2014). Study of the migration phenomena of specific metals in canned tomato paste before and after opening. Validation of a new quality indicator for opened cans. *Food and Chemical Toxicology*, **69**, 25–31. <https://doi:10.1016/j.fct.2014.03.023>.
- Reilly, C. (2002). Metal contamination of food. Its significance for food quality and human health. *Third edition. Blackwell Science Ltd, Oxford, UK*. 266 pp. ISBN 0-632-05927-3.
- Rončević, S., Benutić, A., Nemet, I., & Gabelica, B. (2012). Tin content determination in canned fruits and vegetables by hydride generation inductively coupled plasma optical emission spectrometry. *International Journal of Analytical Chemistry*, **2012**. <https://doi:10.1155/2012/376381>.
- Sherlock, J.C., Hancox, J.H., & Britton, S.C. (1972). Rate of dissolution of tin from tinplate in oxygen-free citrate solutions, II. Effect of coating porosity, *British Corrosion Journal*, **7** (5), 227-231.
- Yang, H-R., Kim, E-S., Ko, Y-S., Jung K., Kim, J-H., Watanabe, T., Nakatsuka, H., Moon, C-S., Shimbo, S. & Ikeda, M. (2015). Food intake survey of kindergarten children in Korea: Part 2. Increased dietary intake of tin possibly associated with canned foods. *Environmental Health and Preventive Medicine*, **20**, 302–306. <https://doi:10.1007/s12199-015-0466-2>.
- Tošković, D.V., Rajković, M.B. & Stanojević, D.D. (2005). Impact of additives on corrosion rate of cans filled with pieces of apricot. *Journal of Agricultural Sciences*, **50**(1), 61–73. <https://doi:10.1007/s12199-015-0466-2>.

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

513

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

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

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

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)