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Simultaneous migration of bisphenol compounds and trace metals in canned vegetable food

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25 trend, with clear influence of storage time, and to a lesser extent of food type. Overall Fe and
26 BADGE·2H₂O migration were favored in acidic food.

27 **Key words:** coated cans; heat treatment; food safety; food storage; migration; Principal
28 Component Analysis (PCA)

29

30 **1. Introduction**

31 In recent years, changes in lifestyle have increased the need of ready-to-eat food and
32 canned/package foods. Among the latter, canned food products offer several advantages,
33 either for the producers or the consumers, namely ease of packaging, sterilizing, handling,
34 transportation and preserving anaerobic environment of the food products (Parkar and
35 Rakesh, 2014). In the meantime, the use of metal cans has to be carefully considered where it
36 occasionally develops integrity problems due to corrosion which can lead to the migration of
37 metal ions (Abdel-Rahman, 2015). To prevent corrosion and food contamination, metallic
38 cans are commonly coated with a thin polymeric film on their inner surface. Yet, it is now
39 well documented that polymerization of lacquer may not be fully complete and that a
40 significant amount of unreacted compounds can be released in food packaged in coated cans
41 (Errico et al., 2014). Indeed, migration from packaging materials is of great concern due to
42 possible adverse health effects (Wagner, Castle, Oldring, Moschakis and Wedzicha, 2018).

43 Several trace metals are prone to migrate, among them tin, iron, lead, cadmium, chromium,
44 nickel, zinc and copper being considered as the most common since they are often used in
45 metal containers. In particular, low levels of tin are currently found in foods and beverages
46 packaged in unlacquered or partially lacquered tinplate cans (Arvanitoyannis and
47 Kotsanopoulos, 2014). Also, iron is the basic element in the steel layer of food cans, while

48 cadmium, nickel and copper may be found as alloying elements in steel. Furthermore,
49 chromium treatment is widely applied to make the tin layer in tinplate cans less susceptible to
50 oxidation damage and to improve the enamel adherence (Arvanitoyannis and Kotsanopoulos,
51 2014). Cr is also usually used in can lids. Likewise, zinc could be present to enhance tin and
52 steel resistance to corrosion (Cederber et al., 2015). Finally, lead is often found in metal
53 packages, so that it is one of the most important contaminants derived from packaging
54 materials (Petropoulos, Raptopoulou, Pasias, Thomaidis and Proestos, 2018). Accordingly,
55 the resolution of Council of Europe on metals and alloys used in food contact materials and
56 articles has reported the need for specific release limits (SRLs) for several trace metals to
57 limit food contamination (Council of Europe, 2013). In addition, due to their toxicity, Sn, Pb
58 and Cd are routinely determined in foodstuffs under the requirements of the European
59 Regulation n°1881/2006.

60 Besides trace metals, organic migrants are also of great concern. Common coating materials
61 for food cans are epoxy resins, with possible migration of several bisphenol compounds.
62 Indeed, bisphenol A diglycidyl ether (BADGE) is a key building block of epoxy resins (upon
63 reaction of bisphenol A (BPA) with epichlorhydrin). Yet, migration studies from epoxy-
64 phenolic coated cans with aqueous foods or food simulants have shown that the migrant
65 BADGE rapidly undergoes hydrolysis to BADGE·H₂O and/or BADGE·2H₂O (Wagner et al.,
66 2018). Moreover when BADGE is used as a scavenger for hydrochloric acid or in the
67 presence of salty food, BADGE·HCl, BADGE·HCl·H₂O and/or BADGE·2HCl are formed.
68 Similar derivatives are obtained when bisphenol F diglycidyl ether (BFDGE) is used (being
69 synthesized from bisphenol F (BPF) as an alternative to BPA). Due to their possible
70 endocrine disrupting effects, bisphenol compounds have been regulated with specific
71 migration limits (SMLs) established for plastics and coatings that are intended to come in

72 contact with foods. For example, the SML of BPA was fixed to 600 µg/kg by European
73 regulation (EU) n°10/2011, being recently reduced to 50 µg/kg according to amendment
74 n°2018/213 (with application on September 6th 2018).

75 Many factors affect the migration from tinfoil cans. In previous studies it was proved that
76 there is a strong correlation between storage time and migration of several metals (Buculei,
77 Armariei, Oroian, Gutt, Gaceu & Birca, 2014; Buculei, Gutt, Sonia and Adriana, 2012;
78 Kassouf, Chebib, Lebbos and Ouaini, 2013; Parkar and Rakesh, 2014; Petropoulos et al.,
79 2018). More specifically, there is significant migration of Sn when cans are not coated with
80 plastic film layer (Pasiadis, Papageorgiou, Thomaidis and Proestos, 2012); in this case high
81 contact temperature seems to accelerate the corrosion of unlacquered cans (Blunden and
82 Wallace, 2003; Parkar and Rakesh, 2014). On the other hand, sterilization was shown to have
83 predominant effect on the migration of bisphenol compounds (Wagner et al., 2018). Other
84 factors, including nature of food [pH (Benitez, Cirillo, Gines and Egli, 2006; Errico et al.,
85 2014; Parkar and Rakesh, 2014), fat content, presence of oxidizing agents and nitrates
86 (Abdel-Rahman, 2015), etc.], type of steel (Blunden & Wallace, 2003), tin coating thickness
87 and surface defects (Benitez et al., 2006), lacquer properties [type (Buculei et al., 2012;
88 Geueke, 2016), thickness (Buculei et al., 2014; Wagner et al., 2018), porosity (Buculei et al.,
89 2014; Wagner et al., 2018), etc.] and volume of headspace (Abdel-Rahman, 2015; Blunden
90 and Wallace, 2003; Parkar and Rakesh, 2014), can significantly affect the migration of metals
91 and/or bisphenol compounds. To our best knowledge, no study has ever combined the
92 analysis of both types of contaminants from tinfoil cans, probably due to different analytical
93 methods required. Yet, organic and inorganic contaminants behave differently, so that
94 conditions prevailing to their migration may differ. In addition, bisphenol and trace metals
95 levels in food should be anti-correlated since trace metal migration is prevented by the
96 presence of organic coating that may release bisphenols. Accordingly, the current work

97 highlights the influence of several parameters (heat treatment, storage time and temperature,
98 food content, can denting, brand, packaging and cooking food cans) on the migration of both
99 inorganic (Sn, Fe, Cr, Cd, Pb, Ni, Cu and Zn) and organic contaminants (BPA, BPF, BPS,
100 BADGE and BFDGE as well as their di-hydrolysis and di-chlorinated derivatives) from
101 coated tinplate cans into food products. Several Lebanese vegetable food products, frequently
102 canned and consumed worldwide, have been considered in this work. [This work studies for](#)
103 [the first time the simultaneous migration of trace metals and bisphenol compounds, enabling](#)
104 [to point out common trends.](#)

105 **2. Materials and methods**

106 ***2.1. Reagents and standards***

107 *2.1.1. Analysis of bisphenol compounds*

108 Acetonitrile (ACN) (HPLC plus gradient grade and LC-MS grade), water (LC-MS grade),
109 methanol (LC-MS grade), ethanol (anhydrous absolute), acetic acid (RPE glacial), formic
110 acid (FA) (LC-MS grade) and ammonium formate (LC-MS grade) were obtained from Carlo
111 Erba (France). BPA (purity grade $\geq 99.9\%$), BPF (purity grade $\geq 98\%$), BPS (purity grade
112 $\geq 98\%$), BADGE (purity grade $\geq 95\%$), BADGE.2H₂O (purity grade $\geq 97\%$), BADGE.2HCl
113 (purity grade $\geq 95\%$), BFDGE (mixture of diastereomers, purity grade $\geq 95\%$), BFDGE.2H₂O
114 (purity grade $\geq 95\%$) and BFDGE.2HCl (total assay of the three isomers, purity grade $\geq 90\%$)
115 were all obtained from Sigma Aldrich (France). Ultra-pure Milli-Q water (18.2 M Ω , 25°C)
116 was produced by an Integral 3 water purification system from Millipore®.

117 *2.1.2. Analysis of metal elements*

118 All reagents used were of analytical grade. Individual standard solutions were freshly
119 prepared through dilution of stock solutions with ultrapure water. Solutions of iron, tin, lead

120 and zinc were prepared from $1,000 \pm 4$ mg/L stock solutions from Fluka Analytical (Buchs,
121 Switzerland), cadmium solutions were from 1,000 mg/L stock solutions from Certipur
122 (Darmstadt, Germany), copper solutions were from 1,000 mg/L stock solutions from Acros
123 Organics (New Jersey, USA), chromium solutions were from 1,000 mg/L stock solutions
124 from Alfa Aesar (Kandel, Germany) and finally nickel was 1,000 \pm 10 mg/L stock solutions
125 from HACH (Dusseldorf, Germany). KCl buffer was prepared from 99.5% pure KCl from
126 AnalaR (England) while strontium was purchased from Merck (Darmstadt, Germany) with
127 purity >99%. Microwave digestion was performed with nitric acid (69%; AnalaR, England)
128 and hydrogen peroxide (30-31%; Sigma Aldrich, USA). All glassware was soaked in nitric
129 acid (1%) overnight and then rinsed with ultra-pure water before use.

130 *2.2. Processing and storage conditions of food samples*

131 A total of 177 food products, including canned “fava beans”, canned “red beans”, canned
132 “chickpeas”, canned “okra” and glass jars of “okra”, were purchased from local industries
133 and supermarkets in Lebanon. Their main characteristics along with their storage time and
134 temperatures during this study are detailed in **Table 1**. Products of brands A and B were
135 totally different Lebanese products, from fabrication of packaging to the filled food. Brand D
136 chickpeas were filled in Lebanon but cans were imported, whereas brand C fava beans were
137 an imported product. Cans of the same product showed the same lot numbers. All cans had
138 white coatings, which was informed from industries to be epoxy-phenolic coating.

139 Canned products of brand A were analyzed from prior to heat treatment (raw food) up to their
140 shelf life of two years (730 days) after heat treatment. As non-heated cans were directly
141 emptied after canning, the contact time between the food and the can was very short, so that
142 we may consider these can contents as raw foods. Still, as the cans were filled by boiling, we
143 cannot exclude a slight release of contaminants from can coating. Heat treated cans were

144 either sterilized (120°C for 30 min - canned legumes, i.e. fava beans, red beans and
145 chickpeas) or pasteurized (100°C for 20 min - canned okra).

146 Okra glass jars (also pasteurized) were examined within the time interval 90 to 330 days.
147 Likewise, legumes from other brands were analyzed between purchase date (i.e. 165 days
148 after production) and until 493 days. Furthermore, to test the influence of storage
149 temperature, a set of canned fava beans and okra (both of brand A) were stored either in
150 refrigerator ($5 \pm 1^\circ\text{C}$), at room temperature ($22 \pm 4^\circ\text{C}$) or in an oven ($40 \pm 2^\circ\text{C}$). For each
151 experiment, three cans were considered.

152 Another set of canned fava beans and okra (both of brand A) were willingly dented and
153 stored at 22°C to simulate the effect of can damages during bad transport and storage in shops
154 or in the house. All collected cans (dented and undamaged) had the same date of production
155 and were stored under the same conditions.

156 Finally three cans of fava beans (brand A), stored for 493 days at 22°C, were opened and
157 heated close to boiling for 3 min, in order to mimic the practical food heating in the can
158 during meal preparation. Canned fava beans were selected for this test since it was judged
159 that they might be heated directly in the can by the consumer as a usual practice.

160 ***2.3. Sample preparation***

161 Each time a can was opened and emptied for analysis, the aspect of can and its food content
162 was carefully examined by naked eye. Generally, the appearance of food and their cans was
163 normal over the studied time and temperature periods. For regular cans, the only worrying
164 appearance was noticed in canned okra samples stored at 40°C for 730 days, with slight
165 rusting appearing on the can external walls and okra pieces showing darker color. In the case

166 of dented cans, no cracking or flaking of the inner coating was observed; a small corrosion
167 was noticed around the external side seam for dented okra cans at 493 days and beyond.

168 The whole food content of three cans (or glass jars), of same lot number, was homogenized in
169 a stainless steel blender. Two analytical procedures were then carried out, either for the
170 extraction of bisphenol compounds or for metals dissolution from the food samples.

171 2.3.1. Bisphenol compounds extraction from food

172 About 100 g of the food mixture was freeze dried using a Labanconco freeze dryer. Three
173 replicates of 0.2 g subsample were taken from each sample and vortexed with 4 mL of
174 methanol (Munguia-Lopez, Peralta, Gonzalez-Leon, Vargas-Requena and Soto-Valdez,
175 2002) then shaken for 20 min and finally soaked for 12 h. After soaking, the samples were
176 shaken again for 20 min. After ensuring the good separation between liquid and solid
177 portions, 3 mL of liquid part were taken and another 3 mL of methanol were added. The
178 mixture was shaken for final 20 min, then a second 3 mL were collected from the liquid
179 phase. The total collected portions (i.e. 6 mL) of methanolic extracts were then evaporated to
180 dryness under gentle nitrogen flow at 35°C. The dried residues were reconstituted with 10
181 mL of ACN/water (5/95 v/v). Further clean-up on Supelco-HLB (60 mg/3 mL) cartridges was
182 performed on a SPE manual VisiprepTM system. Conditioning was achieved successively with
183 5 ml of ACN and 5 ml of ACN/water (5/95 v/v). After sample percolation, washing was
184 ensured with 4 mL of water and 5 mL of ACN/water (5/95 v/v). The target analytes were then
185 eluted with 4 mL ACN. The final extract was evaporated to dryness under gentle nitrogen
186 stream at 35°C. Then, the residues were recovered with 1 ml of chromatographic mobile
187 phase. The final sample solution was diluted three folds (or more if necessary) and further
188 filtrated using 0.2 µm PTFE syringe-less hand compressor filters (Whatman® Mini-UniPrep)
189 before further analysis.

190 *2.3.2. Bisphenol compounds extraction from empty tinplate cans*

191 In order to assess the maximum extractable content of unreacted bisphenol compounds
192 present in the can coating, Paseiro-Cerrato et al. (Paseiro-Cerrato, DeVries and Begley, 2017)
193 suggested that acetonitrile extraction could be performed. Here two cans from brand A were
194 soaked with ACN for 24 and 48 h at room temperature. Since insignificant difference was
195 observed between the two durations, solvent extraction of unreacted bisphenol compounds
196 was carried through soaking for 24 h.

197 *2.3.3. Dissolution of trace metals*

198 The method was previously developed and validated on chickpeas (Kassouf et al., 2013).
199 Three replicates of 2 g fresh homogenized samples (no freeze drying was performed) were
200 accurately weighed into a modified polytetrafluoroethylene (PTFE-TFM) microwave bomb
201 vessel. After adding 7 mL of nitric acid and 1 mL of hydrogen peroxide, the sample digestion
202 was performed in a high-performance microwave digestion system (Anton Paar, Multiwave
203 3000, Graz, Austria) according to the previously described program (Kassouf et al., 2013).
204 The final clear digest was then diluted to 50 mL with ultra-pure water and filtered with 4 µm
205 PTFE filters for subsequent analysis. During the analysis of some elements, the samples were
206 further diluted to remain within the linearity range.

207 *2.4. Analysis of the studied contaminants*

208 *2.4.1. Analytical instruments and conditions for bisphenol compounds*

209 A UHPLC Agilent® 1260 Infinity Series system equipped with a multi-wave fluorescence
210 detector was used for quantification of bisphenol compounds. The system was accompanied
211 with an auto-sampler maintained at 10°C; the injected volume was set at 20 µL.
212 Pentafluorophenyl grafted octadecyl silica column (C18-PFP, 150*2.1 mm ID, 2 µm particle

213 size) was used for the separation of analytes at constant temperature of 20°C. The mobile
214 phase, consisting of Milli-Q water (A) and HPLC plus gradient ACN (B), was pumped at a
215 flow rate of 0.3 ml/min with the following binary gradient: 0 min - 43% B, 1 min ramp to
216 50% B (maintained for 4 min), 2 min ramp to 60% B (maintained for 5 min), 1 min ramp to
217 100% B (maintained for 2 min) and back to 43% B in 1 min (total duration 16 min). The
218 excitation and emission wavelengths of fluorescence detection were set at 230 nm and
219 316 nm respectively. Calibration was performed [using the classical standard addition](#)
220 [approach](#) and [external](#) aqueous solutions. The results obtained showed no difference between
221 the two approaches indicating no matrix effect. Accordingly, quantification was performed
222 with external calibrations of integrated peak areas of eight standard solutions in the range 0.5
223 to 250 µg/L. The instrumental repeatability was ensured through replicate injection of
224 calibration standards: relative standard deviations (%RSDs) ranged from 0.45 to 5% for the
225 inter-day precision tests (n=7), and from 0.15 to 6.2% for the intra-day precision (n=3) tests.

226 For bisphenol compound confirmation, a UHPLC XEVO G2S® (Waters) system equipped
227 with a time-of-flight mass spectrometry detector (TOF-MS) was used. Both ESI- and ESI+
228 ionization modes were operated. The ESI- operation parameters and mobile gradient were as
229 previously described (Noureddine El Moussawi, Karam, Cladière, Chébib, Ouaini & Camel,
230 2017), while ESI+ conditions differed. ESI+ operation parameters were: capillary voltage 1
231 kV; sample cone and source offset 60 and 100 a.u, respectively. Mobile phase composition
232 for ESI+ was: solvents A (LC-MS water/FA 99.9/0.1 v/v) and B (LC-MS ACN/FA 99.9/0.1
233 v/v) pumped with the same gradient used for UHPLC-fluorescence system at column
234 temperature of 30°C. Details of major ions observed for confirmation of bisphenol
235 compounds are indicated in [Supplementary material Table S1](#).

236

237 *2.4.2. Analytical instruments and conditions for trace metals*

238 For analysis of trace metals, atomic absorption spectrometry (AAS) was used. Fe, Sn, Zn and
239 Cu were analyzed on flame AAS (FAAS), while the analysis of Pb, Cd, Cr and Ni was
240 carried on graphite furnace AAS (GFAAS). The FAAS system used was a Thermo Electron
241 Corporation atomic absorption spectrometer with Thermo Solaar (version 10.11) data
242 acquisition software, and the GFAAS system was a Shimadzu AA-6800 atomic absorption
243 spectrometer with WizaArd data acquisition software. The instrumental conditions and
244 matrix modifiers were inspired from the instrument supplementary cookbook and are shown
245 in [Supplementary material Table S2](#). Quantification was performed with external
246 calibration of five points in ranges appropriate for each element (see [Supplementary](#)
247 [material Table S3](#)).

248 *2.5. Method validation*

249 Due to the lack of available reference materials representative of the studied food matrices
250 with the bisphenol compounds, our analytical method on extraction of these compounds from
251 food was validated through recovery tests on spiked unsterilized fava beans and chickpeas.
252 These selected samples were supposed to contain the lowest levels of analyzed compounds
253 (as confirmed by blank analyses of such samples – see results presented below). About 0.2 g
254 of samples were spiked with the target compounds at three levels (low: 100 µg/kg dried food;
255 medium: 400 µg/kg dried food; and high: 1,200 µg/kg dried food), then these samples were
256 vortexed and stored for one hour before extraction as the described method. Recoveries were
257 found satisfactory, ranging from 70 to 120% (see [Supplementary material Table S4](#)).

258 In the case of trace metal analysis, white cabbage certified reference material (BCR[®] -679,
259 Sigma Aldrich, Geel, Belgium) was used to control the accuracy of sample treatment and

260 analysis methods. This reference material contained all targeted elements, except Pb and Sn.
261 Overall, recoveries were in the range 94-111% for all considered trace metals (see
262 [Supplementary material Table S5](#)). The accuracy of the used method for Pb and Sn was
263 previously confirmed by Kassouf et al. (2013) on chickpeas samples.

264 The overall methods limits of detection (MDL) and quantification (MQL) were estimated
265 based on the average signals observed for blank solutions (i.e. blank reagents prepared
266 following both sample preparation methods) plus three and ten times, respectively, the
267 standard deviation of noise on analysis. For bisphenol compounds MDL and MQL values
268 were in the range of 0.26-14.92 µg/kg and 0.31-30.6 µg/kg, respectively (see [Supplementary](#)
269 [material Table S3](#)); hence our method is well appropriate for the analysis of such
270 compounds in food samples since expected concentrations are generally in the 3-500 µg/kg
271 range for most canned foods as already reported (Cao, Corriveau and Popovic, 2010; Gallart-
272 Ayala, Moyano and Galceran, 2011; Sungur, Koroğlu and Özkan, 2014). Performance of our
273 method for trace metals was also satisfactory, with MDL and MQL values in agreement with
274 levels expected in food samples (see [Supplementary material Table S3](#)) (Kassouf et al.,
275 2013; Korfali and Hamdan, 2013; Tuzen and Soylak, 2007). Method precision (RSD),
276 estimated from the standard deviation of validation samples triplicates (spiked or reference
277 material), was in general better than 15%.

278 **2.6. Statistics**

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

282 The multivariate technique of Principal Component Analysis (PCA) was performed in order
283 to examine the correlation between the food content of bisphenol compounds and metals with
284 the studied parameters (type of food and brands, storage time and temperature). The analysis
285 was carried on JMP 14 software. The studied matrix had 129 rows (samples) and 11 columns
286 (variables).

287 **3. Results and discussion**

288 In all our samples (raw and canned foods), despite numerous peaks observed after UHPLC-
289 fluorescence analysis (**Supplementary material Figure S1**), only BPA and BADGE·2H₂O
290 could be confirmed with mass spectrometry, in agreement with previous studies reporting
291 that these two compounds are the most abundant bisphenols in canned food (Sun, Leong,
292 Barlow, Chan and Bloodworth, 2006; Yonekubo, Hayakawa and Sajiki, 2008). Also
293 interestingly, Sn levels remained below detection limit in all our samples, possibly due to the
294 acidic pH working range (3.7-5.9) of our foodstuffs not in favor of Sn dissolution (Benitez et
295 al., 2006), as well as the use of fully lacquered cans (lacquering being expected to decrease
296 Sn release by 99.5%) (Abdel-Rahman, 2015).

297 ***3.1. Occurrence of bisphenol compounds and metals in raw food***

298 BPA was present in most raw foods in the range ND-21.7 µg/kg (see **Supplementary**
299 **material Table S6**), possibly due to food contamination from processing on production line
300 (prior to canning or during can filling) since initial contamination of vegetable food seems
301 rather improbable. On the opposite, BADGE·2H₂O was not detected as expected.

302 For trace metals (see **Supplementary material Table S7**), overall levels are within the
303 ranges reported for unprocessed vegetables (Akinyele and Shokunbi, 2015; Cederber et al.,
304 2015; Pan, Wu and Jiang, 2016), except for Cr with slightly higher values than reported for

305 canned legumes (0.01-0.08 mg/kg) (Korfali and Hamdan, 2013). Fava beans and red beans
306 had close concentrations of most metals. Among notable differences, Fe and Cu levels were
307 the lowest in okra, while Ni and Cu levels were the highest in chickpeas.

308 *3.2. Effect of the canning process and contaminants levels in unstored canned food*

309 *3.2.1. Effect of the canning process on contaminant migration*

310 The sterilization process led to the migration of both BADGE·2H₂O and BPA into food (see
311 **Figure 1**) as already observed (Cabado et al., 2008; Geens et al., 2012; Goodson, Robin,
312 Summerfield and Cooper, 2004). Considering the cans' dimensions and the initial levels in
313 raw foods, migration due to sterilization was around 12.5-14.7 µg/dm² for BADGE·2H₂O,
314 and 3.9-4.8 µg/dm² for BPA. Interestingly, pasteurization had no noticeable effect on BPA
315 levels (no migration) whereas the highest BADGE·2H₂O level was observed in pasteurized
316 canned okra (migration 23.2 µg/dm²). In that latter case, migration was more influenced by
317 the food properties rather than heat treatment since okra offers conditions that favor rapid
318 BADGE hydrolysis (low pH (3.7) and high water content (93.8%)). This is confirmed by the
319 high percentage (52-94%) of extractable BADGE·2H₂O recovered in our food products rich
320 in water (>70%) (Leepipatpiboon, Sae-Khow and Jayanta, 2005; Munguia-Lopez and Soto-
321 Valdez, 2001). On the opposite, only part (<30%) of extractable BPA was recovered in our
322 canned food samples, far below previous observations reporting 70-100% BPA extraction
323 during sterilization (Paseiro-Cerrato et al., 2017; Goodson et al., 2004).

324 Considering trace metals migration (see **Supplementary material Table S6**), the effect of
325 heat treatment was positively significant in some cases only, with moderate increase (up to
326 17-34%) for Ni, Cu and Zn. Fe levels were most affected for okra (58% increase), despite the

327 mild pasteurization treatment, suggesting that the high acidic nature of this foodstuff plays a
328 major role on increasing Fe content in food during heat treatment (Parkar and Rakesh, 2014).

329 *3.2.2. Contaminants levels in unstored canned food and compliance with the regulation*

330 Our BPA levels for canned food from Lebanese market were in the range 12.8-54.6 µg/kg
331 (see **Table 2**, storage time 0), which is within the low values of ranges reported for canned
332 food from Japanese (ND-235.4 µg/kg) or US (2.6-730 µg/kg) markets (Yonekubo et al.,
333 2008; Noonan, Ackerman and Begley, 2011). The highest BPA value was noted in fava beans
334 from brand C, which is the only brand studied here that was fully packed outside Lebanon,
335 where the canning procedure and packaging materials may greatly differ and therefore
336 influence BPA migration. These levels do comply with the European specific migration limit
337 of 50 µg/kg (European Commission Regulation (EC) n°2018/213), except for brand A canned
338 fava beans with a value slightly above. In the same samples, BADGE·2H₂O was in the range
339 101-146 µg/kg, well within reported range (ND-400 µg/kg) (Yonekubo et al., 2008; Sun et
340 al., 2006) and far below the European specific migration limit of 9,000 µg/kg for the sum of
341 BADGE and its hydrolysis derivatives (European Commission Regulation (EC)
342 n°1895/2005).

343 Among trace metals, the highest levels were observed for Fe and Zn (see **Supplementary**
344 **material Table S6**). Mean Fe contents varied between 5.6 and 14.0 mg/kg (see **Table 2**,
345 storage time 0), in agreement with values reported for canned vegetables (Korfali and
346 Hamdan, 2013). Zn levels were lower (2.2-5.8 mg/kg) and compare favorably with values
347 reported in canned vegetables (i.e. 7.42 mg/kg) and canned legumes (i.e. 12.8 mg/kg)
348 (Korfali and Hamdan, 2013; Tuzen and Soylak, 2007). Ni concentrations (0.06-0.54 mg/kg)
349 are also comparable to levels reported for Jordanian marketed canned green beans (Massadeh

350 and Al-Massaedh, 2017). On the opposite, our Cu levels (0.55-4.42 mg/kg) are slightly higher
351 than previously reported for canned vegetables (average of 1.63 mg/kg) (Korfali and
352 Hamdan, 2013). For both Ni and Cu, the highest levels were found in chickpeas and the
353 lowest in okra. Cr was present in all samples in the range 0.05-0.22 mg/kg (see **Table 2**,
354 storage time 0), the lowest values being observed in brand B fava beans, and the highest in
355 brand A chickpeas.

356 The lowest levels among trace metals were for Cd and Pb. As a matter of fact, Cd levels were
357 unexpectedly low (i.e. < MQL-0.04 mg/kg), where an average level of 0.20 mg/kg was
358 previously noted for Lebanese marketed canned legumes (Korfali and Hamdan, 2013). Yet,
359 our values are within those reported by FAO/WHO (2004) in vegetables for European and
360 Asian countries (i.e. 0.006-0.10 mg/kg). Pb levels were in the range 0.02-0.05 mg/kg (see
361 **Table 2**), being in the lower value of previous range reported for canned legumes from
362 Lebanese market (i.e. 0.05-0.60 mg/kg) (Kassouf et al., 2013; Korfali and Hamdan, 2013).
363 With regard to Cd and Pb levels, all our food samples do comply with the European
364 regulation (European Commission Regulation (EC) n°1881/2006).

365 ***3.3. Contaminants levels in canned foods over storage***

366 Detailed levels measured for all contaminants depending on the food category and brand, as
367 well as storage conditions (time and temperature) are given in **Table 2**. Results from PCA
368 (see **Figure 2**) are helpful for highlighting trends in contaminants migration or release. Three
369 principal components with eigen values > 1 were observed when the contaminant levels,
370 storage time and storage temperature are chosen as variables, explaining 66% of data
371 variance. Interestingly, PC1 is clearly related with food categories (classified as okra, red
372 bean, fava beans and chickpeas), and PC2 with storage conditions (mainly time, but also
373 temperature), whereas PC3 is linked both to the brand and storage temperature.

374 *3.3.1. General patterns observed*

375 Several groups can be distinguished based on PCA results. Clearly Cd, Ni and Cu behave the
376 same, with their levels linked to the food type (the highest being observed in chickpeas) and
377 brand. BADGE·2H₂O, Fe and Cr may be gathered in another group, even though some
378 discrepancy of their behavior is evident, with clear influence of storage, and to a lesser extent
379 of food type and brand. Then, BPA and Zn show similar pattern, their levels being mainly
380 correlated with food type and brand as well as storage temperature; as a matter of fact, as
381 BPA, Zn can be affected by the coating composition since zinc oxide is often added to the
382 lacquer in order to absorb odorous sulfides liberated during and after heat treatment. Pb
383 migration trend is very similar, but its level is additionally influenced by storage time.

384 *3.3.2. Effect of food category*

385 As discussed previously, the highest BADGE·2H₂O and Fe levels are noted in the case of
386 pasteurized okra for unstored canned foods, due to the specificities of this food category
387 (highly acidic pH and aqueous) that favors release of both contaminants. Similar observation
388 can be drawn upon canned food storage since their levels increase over storage in okra
389 whatever the storage conditions. In fact, okra samples are clearly separated from other food
390 samples on PC1 as shown in **Figure 2**, and the highest increase levels over storage are also
391 noted for BPA and Zn, and to a lesser extent Cr and Ni. For trace metals we may assume that
392 acidic pH favors their dissolution from the can and subsequent release. In the case of BPA, it
393 is probably linked to the mild pasteurization. Part of residual BPA could have remained on
394 the coating after pasteurization and then mass transfer is completed during storage time.
395 Similar results were reported for BPA upon pasteurization of canned jalapeno peppers
396 (Munguia-Lopez and Soto-Valdez, 2001). Accordingly, okra samples exhibited the highest
397 dispersion on PC2 linked to storage conditions.

398 As expected, pasteurized okra contained in glass jars exhibited lower levels of bisphenols
399 (both BPA and BADGE·H₂O not detected) as well as lower contents of Fe. Hence minimal
400 release of Fe was observed between 90 and 330 days (but Fe level still increased by 25%,
401 probably coming from the lid). So, glass jars appears as a safer packaging with regards to
402 chemical contaminants release.

403 *3.3.3. Effect of storage conditions*

404 While the PCA results highlight general trends based on the maximum dispersion of values,
405 the univariate analyses (see **Table 2**) enable to point out low but significant variations of
406 concentrations in order to differentiate the behaviors of compounds over storage conditions.
407 Several contaminants were affected by storage, and two different migration patterns could be
408 distinguished: fast release of contaminants followed by stabilization for prolonged storage, or
409 slow release along the shelf life. For some contaminants, no clear pattern could be
410 distinguished. In addition, few contaminants remained unaffected over storage.

411 *Contaminants exhibiting fast release followed by stabilization*

412 BADGE·2H₂O is characterized by a rapid migration during the first half of shelf life (0-330
413 days) for most food products and can types, followed by a stabilization of its concentrations
414 for prolonged durations (330-730 days) according to **Table 2**. As an example, for canned fava
415 beans of brand A, BADGE·2H₂O level rises from 119 ± 25 µg/kg at day 0 to approximately
416 150 ± 10 µg/kg at 330 days (22°C), remaining constant up to 493 days (22°C). The high
417 quantity of BADGE in the can inner lacquer may favor its rapid hydrolysis and release into
418 our aqueous food products during the first days of storage, while an equilibrium is rapidly
419 reached and as a consequence limits its migration.

420

421 *Contaminants exhibiting slow-release*

422 The second pattern of migration is observed for Cd, Ni and Cu (as illustrated in **Figure 2**),
423 depicted by quite constant concentrations during the first half of shelf life followed by
424 significant small concentration increases during the second half. A typical illustration is given
425 by Cu in fava beans (see **Table 2**): its level of around 1.6 ± 0.1 mg/kg during the 0-493 days'
426 period increased up to 2.1 ± 0.1 mg/kg at 730 days. In any case, Cu release remained below
427 the recommended SRL (i.e. 4 mg/kg) (Council of Europe, 2013). Interestingly, levels
428 observed were not influenced by storage temperature whatever the food types or brands. In
429 practice, Cd, Ni and Cu can be found as alloying elements in steel. Their migration pattern
430 may be linked to their reduced concentrations in the can metal alloy which limit their
431 migration, resulting in a slow-release over time.

432 *Contaminants with unclear behavior under our tested conditions*

433 Fe and Zn display unclear migration pattern, their behavior being dependent on the food
434 products or brand (**Table 2**); as a matter of fact, different behaviors for Fe release were also
435 previously noted depending on the food canned (Parkar and Rakesh, 2014). These elements
436 face a fast release and stabilization in some foodstuffs (red beans and chickpeas for Fe; brand
437 A fava bean for Zn). Previous report also mentioned the fast release of Fe in canned foods
438 (Kassouf et al., 2013). However, we also notice their slow release in other samples (brand B
439 fava beans for Fe; brand C fava beans and chickpeas for Zn). Noticeably, the higher the
440 storage the temperature, the higher the Fe levels as already observed (Parkar and Rakesh,
441 2014). Fe is a main constituent of the cans, and the presence of citric acid in most of our
442 foodstuffs (see **Table 1**) may favor its release, since citric acid tends to solubilize iron (Chu
443 and Wan, 1993). On the other hand, Zn is found in the metal alloy (possibly resulting in slow

444 migration) and its oxide is frequently added to the lacquer (possibly explaining the fast
445 release observed in some samples).

446 *Contaminants slightly affected or unaffected*

447 According to **Table 2**, several contaminant levels remained unchanged whatever the storage
448 conditions. In particular, Pb level in most our food products was stable and not affected,
449 neither by heat treatment nor by storage, except in brand B fava beans cans stored over 493
450 days where it significantly increased (probably due to the presence of Pb as impurity in the
451 can alloy). By way of consequence, in such a case, Pb concentrations were close to the
452 European maximum permitted levels in legumes (i.e. 0.2 mg/kg) but still remaining below the
453 maximum level allowed (i.e. 1 mg/kg) in canned beans according to the Codex Alimentarius
454 (Codex Stan 193-1995) and Libnor (Libnor, 1999), and the corresponding Pb release values
455 exceed the recommended SRL (i.e. 0.01 mg/kg) (Council of Europe, 2013). Cr behaves quite
456 similarly as Pb, but in addition slight increases in its level are noticeable upon storage of
457 brand A canned fava beans and red beans, possibly linked to the use of Cr as a protective
458 layer to prevent tin oxidation for these brand A cans.

459 Apart from okra, in other foods BPA was also slightly affected by storage conditions as
460 shown in **Table 2**. Its migration pattern is not clear since its concentrations tend to slightly
461 decrease over time. One explanation is that migration is driven by the quantity of free BPA
462 initially present in the cans, where the equilibrium is probably reached during sterilization.
463 Then slight changes in its levels could be attributed to the inter-cans variability rather than to
464 storage conditions. Stability of BPA levels in sterilized canned foods over storage time has
465 been also reported (Munguia-Lopez and Soto-Valdez, 2001; Nouredine El Moussawi et al.,
466 2017; Paseiro-Cerrato et al., 2017).

467

468 **3.4. Effect of can denting**

469 Damage to the can, in the form of denting, had no appreciable effect on the migration of BPA
470 and BADGE·2H₂O in canned fava beans, which is in agreement with results reported for
471 BPA migration in non-acidic canned food (Goodson et al., 2004). At certain times, elements
472 like Fe, Ni, Cu and Zn showed a slight decrease upon denting (see **Table 3**). This unexpected
473 decrease could be related to antioxidants (such as EDTA) present in fava beans (brand A) that
474 can form strong complexes with metal ions. For acidic okra, we observed a significant release
475 of BADGE·2H₂O, Fe, Cu and Cd at both storage durations, probably due to corrosion
476 resulting in can damage (the highest effect was observed on Fe, with release enhanced by 86-
477 90% and subsequent Fe level of 61.9 mg/kg at 730 days). So, undamaged food cans are
478 preferable over dented cans, especially in case of highly acidic food.

479 **3.5. Influence of consumer practices: effect of heating food directly in the can**

480 Overall, no significant effect of this practice was noticed on the considered contaminants
481 levels in the canned fava beans (see **Table 4**). Similar conclusions were drawn for BPA in a
482 previous study (Goodson et al., 2004), while to our best knowledge the effect of heating food
483 directly in the cans has never been investigated for trace metals before. So, our results do
484 confirm that, under the tested conditions, this practice is safe concerning the migration of
485 potentially toxic metals and bisphenol compounds.

486 **4. Conclusion**

487 This work highlights for the very first time the main factors that influence the simultaneous
488 migration of trace metals and bisphenol compounds from coated tinplate cans into vegetable
489 foods. Sn was undetected in all our samples, which may be attributed to the presence of
490 lacquer as well as unsuitable food pH for its dissolution. All other considered metals were

491 found, with some samples that did not comply with the European regulation, either due to
492 levels being above the maximum values authorized in food (e.g. Pb in canned chickpeas of
493 brand D) or to release being above the SRL value (e.g. Fe in canned okra stored at 40°C
494 beyond 493 days, and in dented okra cans). Among bisphenols, only BPA and BADGE·2H₂O
495 were confirmed in our samples; in a few samples (e.g. brand C fava beans) BPA migration
496 was found to exceed its SML value recently set by the European regulation. Our study
497 confirms that sterilization is the main contributing parameter for the migration of free
498 bisphenol compounds (here release less than 80% of maximum free bisphenol compounds
499 was observed); heat treatment in food glass jars should be preferred, as undetected levels of
500 all bisphenol compounds were found in that case. Our PCA results suggest several trends of
501 migration depending on the contaminants. Interestingly, the primary hypothesis that
502 bisphenols and trace metals levels in food should be anti-correlated is invalid based on these
503 results. Besides, the fact that BPA and Zn (and Pb to a lesser extent) have similar trends is
504 interesting and shown for the first time. This suggests that their migration is affected by can
505 composition and coating. In addition, food pH and water content seem to play a major role in
506 favoring migration. Surprisingly, for non-acidic food, can denting as well as cooking food in
507 cans showed no effect on the migration of inorganic or organic targeted migrants. On the
508 other hand, in case of acidic food (namely okra), several recommendations can be drawn for
509 industries and consumers: (i) to store cans under moderate temperature to limit excessive
510 release of Fe and BADGE·2H₂O; (ii) to discard dented cans since high release of Fe is
511 expected; (iii) to control the purity of metal substrate as well as the polymerization and
512 formulation of polymeric coating, since our results confirm major differences in the
513 packaging quality between brands.

514

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519

520 **6. Declaration of interest**

521 None

522

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658 **8. Figure captions**

659 **Figure 1:** Impact of heat treatment on BPA and BADGE·2H₂O levels in brand A canned
660 food products (sterilized foods, except pasteurized okra).

661 **Figure 2:** Scores and loadings on the combination of PC1 and PC2 (a), PC2 and PC3 (b),
662 PC1 and PC3 (c) resulting from PCA applied on all our data.

663

664 **9. Appendix A. Supplementary material**

665 **Table 1:** Detailed information of the studied food products.

Product	Brand	Package	Production country	Net weight (g)	Can size (height* diameter) (cm ²)	Free space (cm)	pH ^a	Moisture (%) ^b	Fat (% w/w) ^c	Antioxidants ^c	Storage temperature (°C)	Storage time (days)
Fava beans	A*	Cans	Lebanon	400	10*7.5	0.5	5.9	79.8 ± 0.9	1	EDTA ^e (E385) Sodium metasilfite (E223)	5 ± 1 22 ± 4 40 ± 2	0 to 730
	B	Cans	Lebanon	600	11.5*8.5	0.4	5.9	80.4 ± 0.3	unknown	EDTA (E385) Citric acid (E330)	22 ± 4	purchase date + 493
	C	Cans	UAE**	400	10*7.5	0	5.6	72.7 ^f	0.8	EDTA (E385) Citric acid (E330)	22 ± 4	purchase date + 493
Chickpeas	A*	Cans	Lebanon	400	10*7.5	0	5.1	78.8 ± 6.9	2.5	EDTA (E385) Citric acid (E330)	22 ± 4	0 to 730
	D	Cans	Lebanon	400	10*7.5	0	5.2	79.0 ^f	2.4	EDTA (E385) Citric acid (E330)	22 ± 4	purchase date + 493
Red beans	A*	Cans	Lebanon	400	10*7.5	0.3	5.7	76.1 ± 0.8	0.5	EDTA (E385) Citric acid (E330)	22 ± 4	0 to 730
Okra	A*	Cans	Lebanon	820	11.6*10	0.2	3.7	93.8 ± 0.3 ^d	0.3	Citric acid (E330)	5 ± 1 22 ± 4 40 ± 2	0 to 730
		Glass jars	Lebanon	660	11.5*8.5	0	3.9		0.3	Citric acid (E330)	22 ± 4	90 to 330

666 * Vacuum packed, ** United Arab Emirates

667 ^a Determined by pH meter, ^b Determined from freeze drying where the difference in mass before and after drying is calculated

668 ^c According to product label, ^d For both cans and jars

669 ^e Ethylene diamine tetraacetic acid, ^b Determined from lyophilization

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678 **Table 2:** Levels of bisphenols and metals in canned foods, and evolution during storage.

Food type	Storage time (days)	Storage temperature (°C)	Compound or element (conc. ± SD)								
			BPA	BADGE·2H ₂ O	Fe	Pb	Cd	Cr	Ni	Cu	Zn
			μg/kg		mg/kg						
Fava beans (brand A)	0*	-	54.60 ± 2.62 ^a	119.37 ± 25.07 ^a	10.73 ± 0.17 ^a	0.03 ± 0.00 ^a	0.01 ± 0.00 ^a	0.12 ± 0.01 ^a	0.3 ± 0.02 ^a	1.62 ± 0.04 ^a	5.83 ± 0.07 ^a
	75 ± 18	22 ± 4	55.81 ± 6.98 ^a	168.87 ± 26.16 ^b	8.79 ± 1.01 ^b	0.03 ± 0.00 ^a	0.01 ± 0.00 ^a	0.14 ± 0.01 ^a	0.31 ± 0.01 ^a	1.55 ± 0.11 ^a	7.32 ± 0.18 ^b
		5 ± 1	46.67 ± 1.68 ^b	154.87 ± 16.41 ^b	10.92 ± 0.25 ^a	0.03 ± 0.00 ^a	0.01 ± 0.00 ^a	0.16 ± 0.00 ^b	0.36 ± 0.00 ^a	1.46 ± 0.10 ^a	7.30 ± 0.17 ^b
	330 ± 24	22 ± 4	48.49 ± 1.50 ^b	152.34 ± 3.20 ^b	10.77 ± 0.19 ^a	0.03 ± 0.00 ^a	0.01 ± 0.00 ^a	0.16 ± 0.00 ^b	0.40 ± 0.01 ^b	1.78 ± 0.16 ^a	7.16 ± 0.28 ^b
		40 ± 2	63.63 ± 9.03 ^c	193.36 ± 5.42 ^c	13.80 ± 0.01 ^c	0.03 ± 0.00 ^a	0.01 ± 0.00 ^a	0.16 ± 0.00 ^b	0.43 ± 0.01 ^c	1.65 ± 0.02 ^a	6.68 ± 0.67 ^b
	493 ± 38	5 ± 1	39.75 ± 2.47 ^d	112.12 ± 13.91 ^a	10.51 ± 0.37 ^a	0.03 ± 0.00 ^a	0.02 ± 0.00 ^b	0.14 ± 0.00 ^a	0.34 ± 0.03 ^a	1.84 ± 0.07 ^a	6.56 ± 0.37 ^c
		22 ± 4	50.53 ± 2.63 ^{a,b}	141.00 ± 11.60 ^{a,b}	13.06 ± 0.50 ^d	0.03 ± 0.00 ^a	0.02 ± 0.00 ^b	0.15 ± 0.00 ^b	0.38 ± 0.01 ^b	1.75 ± 0.05 ^a	6.99 ± 0.18 ^{b,c}
	730	40 ± 2	47.63 ± 1.90 ^b	149.14 ± 14.92 ^{a,b}	15.33 ± 0.08 ^e	0.03 ± 0.00 ^a	0.02 ± 0.00 ^b	0.15 ± 0.01 ^b	0.38 ± 0.00 ^b	1.86 ± 0.06 ^a	6.72 ± 0.04 ^c
		5 ± 1	NA	NA	10.38 ± 0.16 ^a	0.03 ± 0.00 ^a	0.02 ± 0.00 ^b	0.14 ± 0.02 ^a	0.37 ± 0.02 ^b	2.13 ± 0.07 ^b	6.48 ± 0.10 ^c
	Fava beans (brand B)	0*	-	24.61 ± 3.59 ^a	116.20 ± 19.78 ^a	5.59 ± 0.32 ^a	0.06 ± 0.01 ^a	0.01 ± 0.00 ^a	0.05 ± 0.00 ^a	0.11 ± 0.00 ^a	2.59 ± 0.04 ^a
75 ± 18		22 ± 4	19.61 ± 4.80 ^a	210.89 ± 15.18 ^a	8.82 ± 0.41 ^b	0.10 ± 0.01 ^b	0.01 ± 0.00 ^a	0.07 ± 0.00 ^b	0.14 ± 0.01 ^b	2.67 ± 0.06 ^a	4.43 ± 0.27 ^a
Fava beans (brand C)	493 ± 38	22 ± 4	NA	NA	11.58 ± 0.94 ^c	0.19 ± 0.01 ^c	0.02 ± 0.00 ^b	0.08 ± 0.00 ^c	0.24 ± 0.01 ^c	2.52 ± 0.18 ^a	4.41 ± 0.02 ^a
Fava beans (brand C)	165 ± 15	22 ± 4	104.42 ± 19.20	181.21 ± 16.30	7.44 ± 0.69 ^a	0.15 ± 0.00 ^a	0.02 ± 0.00 ^a	0.08 ± 0.00 ^a	0.41 ± 0.02 ^a	2.60 ± 0.16 ^a	4.34 ± 0.41 ^a
	493 ± 38	22 ± 4	NA	NA	10.16 ± 0.58 ^b	0.21 ± 0.02 ^b	0.03 ± 0.00 ^b	0.08 ± 0.01 ^a	0.50 ± 0.03 ^b	2.75 ± 0.17 ^a	4.41 ± 0.32 ^a

679 n=3

680 * after sterilization or pasteurization

681 NA: not analyzed

682 Within each contaminant of each food product: a to g correspond to significantly different concentrations (p<0.05), whereas concentrations showing same letter are not

683 significantly different (p>0.05)

684 MQL: method quantification limit

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687 **Table 2 (continued):** Evolution of bisphenol compounds and metals in canned foods as a function of storage time and temperature.

Food type	Storage time (days)	Storage temperature (°C)	Compound or element (conc. ± SD)								
			BPA	BADGE·2H ₂ O	Fe	Pb	Cd	Cr	Ni	Cu	Zn
			µg/kg		mg/kg						
Red beans (brand A)	0*	-	39.95 ± 2.54 ^a	102.58 ± 7.22 ^a	14.04 ± 0.82 ^a	0.02 ± 0.00 ^a	0.01 ± 0.00 ^a	0.14 ± 0.00 ^a	0.29 ± 0.03 ^a	2.09 ± 0.15 ^a	3.67 ± 0.21 ^a
	75 ± 18	22 ± 4	42.34 ± 0.24 ^a	166.41 ± 18.19 ^b	17.70 ± 0.37 ^b	0.03 ± 0.00 ^b	0.01 ± 0.00 ^a	0.14 ± 0.00 ^a	0.36 ± 0.00 ^b	2.09 ± 0.03 ^a	5.71 ± 0.20 ^b
	330 ± 24	22 ± 4	41.50 ± 1.88 ^a	182.99 ± 4.78 ^b	21.09 ± 1.02 ^c	0.03 ± 0.00 ^b	0.01 ± 0.00 ^a	0.16 ± 0.00 ^b	0.37 ± 0.01 ^b	2.26 ± 0.09 ^b	5.61 ± 0.08 ^b
	493 ± 38	22 ± 4	40.57 ± 9.30 ^a	182.36 ± 9.12 ^b	23.33 ± 2.30 ^c	0.02 ± 0.00 ^a	0.01 ± 0.00 ^a	0.16 ± 0.01 ^b	0.31 ± 0.01 ^a	2.20 ± 0.07 ^b	5.92 ± 0.04 ^c
	730	22 ± 4	NA	NA	23.04 ± 2.44 ^c	0.03 ± 0.00 ^a	0.01 ± 0.00 ^a	0.15 ± 0.01 ^b	0.36 ± 0.02 ^b	2.58 ± 0.12 ^c	6.03 ± 0.13 ^c
Chickpeas (brand A)	0*	-	41.06 ± 0.84 ^a	100.96 ± 11.37 ^a	12.23 ± 0.38 ^a	0.02 ± 0.00 ^a	0.04 ± 0.00 ^a	0.22 ± 0.02 ^a	0.54 ± 0.03 ^a	4.42 ± 0.16 ^a	2.98 ± 0.05 ^a
	75 ± 18	22 ± 4	35.55 ± 0.46 ^b	156.95 ± 8.76 ^b	12.09 ± 0.39 ^a	0.02 ± 0.00 ^a	0.04 ± 0.00 ^a	0.24 ± 0.01 ^a	0.58 ± 0.01 ^a	5.09 ± 0.07 ^b	2.31 ± 0.00 ^b
	330 ± 24	22 ± 4	32.10 ± 0.21 ^c	163.37 ± 14.29 ^b	21.86 ± 0.24 ^b	0.02 ± 0.00 ^a	0.04 ± 0.00 ^a	0.25 ± 0.02 ^a	0.70 ± 0.04 ^b	5.68 ± 0.09 ^c	2.38 ± 0.13 ^b
	493 ± 38	22 ± 4	34.21 ± 4.70 ^{a,b,c}	155.78 ± 14.48 ^b	22.03 ± 1.04 ^b	0.02 ± 0.00 ^a	0.04 ± 0.00 ^a	0.24 ± 0.00 ^a	0.63 ± 0.06 ^b	6.13 ± 0.26 ^d	4.61 ± 0.07 ^c
	730	22 ± 4	NA	NA	23.37 ± 1.15 ^b	0.02 ± 0.00 ^a	0.04 ± 0.00 ^a	0.23 ± 0.00 ^a	0.67 ± 0.06 ^b	6.23 ± 0.14 ^d	5.04 ± 0.00 ^d
Chickpeas (brand D)	165 ± 15	22 ± 4	44.24 ± 1.36	88.62 ± 4.58	9.08 ± 0.47 ^a	0.22 ± 0.02 ^a	0.02 ± 0.00 ^a	0.08 ± 0.01 ^a	0.77 ± 0.01 ^a	4.93 ± 0.11 ^a	6.35 ± 0.30 ^a
	493 ± 38	22 ± 4	NA	NA	12.20 ± 1.15 ^b	0.26 ± 0.02 ^b	0.03 ± 0.02 ^b	0.08 ± 0.00 ^a	1.11 ± 0.10 ^b	5.03 ± 0.18 ^a	7.69 ± 0.06 ^b
Okra – Cans (brand A)	0*	-	12.82 ± 1.09 ^a	146.20 ± 5.90 ^a	9.88 ± 0.65 ^a	0.05 ± 0.01 ^a	<MQL	0.13 ± 0.01 ^a	0.06 ± 0.01 ^a	0.55 ± 0.03 ^a	2.21 ± 0.27 ^a
	330 ± 24	22 ± 4	25.44 ± 1.36 ^b	122.07 ± 7.35 ^b	13.11 ± 1.24 ^b	0.05 ± 0.00 ^a	<MQL	0.19 ± 0.00 ^b	0.06 ± 0.00 ^a	0.48 ± 0.01 ^b	2.86 ± 0.19 ^b
	493 ± 38	5 ± 1	26.49 ± 1.95 ^b	169.53 ± 14.33 ^a	12.52 ± 2.02 ^b	0.05 ± 0.00 ^a	<MQL	0.21 ± 0.00 ^c	0.08 ± 0.01 ^b	0.56 ± 0.07 ^a	2.97 ± 0.21 ^b
		22 ± 4	30.28 ± 2.32 ^c	133.79 ± 1.39 ^c	23.21 ± 0.91 ^c	0.05 ± 0.00 ^a	<MQL	0.21 ± 0.00 ^c	0.07 ± 0.00 ^b	0.59 ± 0.03 ^a	3.30 ± 0.22 ^c
		40 ± 2	41.57 ± 1.67 ^d	330.36 ± 7.22 ^d	39.39 ± 1.58 ^d	0.05 ± 0.00 ^a	<MQL	0.21 ± 0.00 ^c	0.10 ± 0.01 ^c	0.59 ± 0.02 ^a	4.23 ± 0.47 ^d
	730	5 ± 1	28.39 ± 1.21 ^{b,c}	134.49 ± 23.17 ^{a,b,c}	26.14 ± 0.97 ^e	0.05 ± 0.00 ^a	<MQL	0.22 ± 0.00 ^c	0.29 ± 0.01 ^d	0.63 ± 0.04 ^c	2.68 ± 0.12 ^b
22 ± 4		32.68 ± 0.18 ^c	130.88 ± 0.37 ^c	33.16 ± 1.76 ^f	0.06 ± 0.01 ^a	<MQL	0.21 ± 0.01 ^c	0.30 ± 0.03 ^d	0.65 ± 0.04 ^c	3.25 ± 0.23 ^c	
Okra – Jars (brand A)	90	22 ± 4	ND	ND	5.47 ± 0.40 ^a	0.04 ± 0.00 ^a	ND	0.16 ± 0.00 ^a	0.10 ± 0.00 ^a	0.52 ± 0.01 ^a	2.79 ± 0.04 ^a
	330	22 ± 4	ND	ND	6.86 ± 0.30 ^b	0.04 ± 0.00 ^a	ND	0.15 ± 0.00 ^a	0.09 ± 0.01 ^a	0.53 ± 0.01 ^a	3.34 ± 0.02 ^b

688 n=3

689 * after sterilization or pasteurization

690 NA: not analyzed, ND: not detected

691 Within each contaminant of each food product: a to g correspond to significantly different concentrations (p<0.05), whereas concentrations showing same letter are not significantly different (p>0.05)

692 MQL: method quantification limit

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695 **Table 3:** Effect of denting fava beans and okra cans on the migration of bisphenol compounds and metal elements.
696

Food	Storage time (days)	Can aspect	Compound or element (conc. ± SD)								
			BPA	BADGE·2H ₂ O	Fe	Pb	Cd	Cr	Ni	Cu	Zn
			µg/kg		mg/kg						
Fava beans (brand A)	330 ± 24	Undamaged	48.49 ± 1.50	152.34 ± 3.20	10.77 ± 0.19	0.03±0.00	0.01±0.0001	0.16±0.00	0.34±0.01	1.78±0.16	7.16±0.28
		Dented	47.16±6.61	153.76±13.38	11.20±0.54	0.03±0.00	0.01±0.0001	0.16±0.00	0.36±0.01*	1.80±0.05	6.71±0.31*
	493 ± 38	Undamaged	50.53 ± 2.63	141.00 ± 11.60	13.06 ± 0.50	0.03±0.00	0.02±0.00	0.16±0.01	0.38±0.01	1.75±0.05	6.99±0.18
		Dented	50.27±4.47	141.85±6.81	10.60±0.23*	0.03±0.00	0.02±0.00	0.14±0.01	0.35±0.02*	1.88±0.08	6.03±0.23*
	720	Undamaged	NA	NA	12.96 ± 0.01	0.03±0.00	0.02±0.001	0.14±0.01	0.35±0.03	2.13±0.07	6.65±0.28
		Dented	NA	NA	10.82±0.18*	0.03±0.00	0.02±0.003	0.13±0.01	0.35±0.01	1.84±0.05*	6.24±0.10*
Okra (brand A)	493 ± 38	Undamaged	30.28±2.32	133.79±1.39	23.21 ± 0.91	0.05±0.00	ND	0.21±0.00	0.07±0.00	0.59±0.03	3.30±0.22
		Dented	33.13±2.73	145.96±0.20*	44.01±4.23*	0.05±0.00	ND	0.21±0.00	0.10±0.01*	0.82±0.04*	3.80±0.20*
	720	Undamaged	32.68±0.18	130.88±0.37	33.16 ± 1.76	0.06±0.01	ND	0.21±0.01	0.30±0.03	0.65±0.04	3.25±0.23
		Dented	28.57±2.18	143.78±3.69*	61.91±0.84*	0.06±0.00	0.01±0.00*	0.21±0.01	0.27±0.03	0.81±0.03*	3.96±0.13*

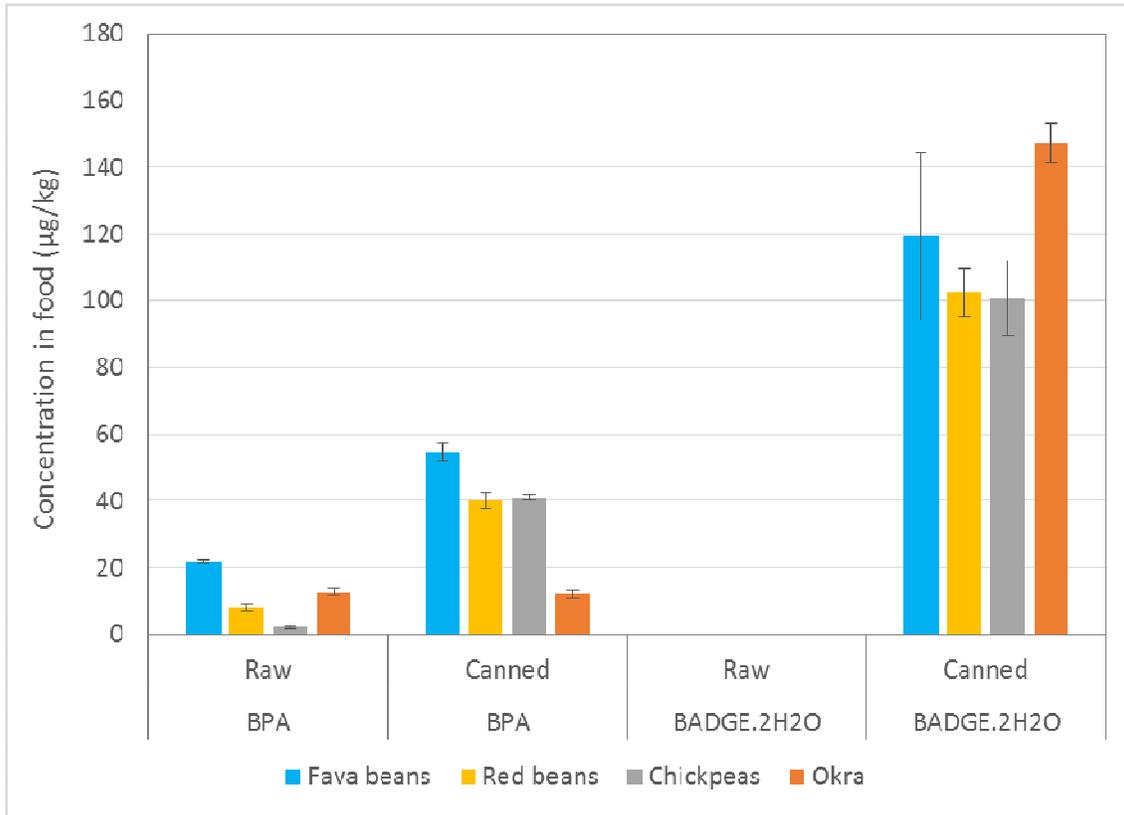
697 n=3
698 NA: not analyzed, ND: not detected
699 * significant difference in concentration is noticed between dented and undamaged cans (p<0.05)

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Table 4: Effect of heating fava beans directly in the cans on the migration of bisphenol compounds and metal elements..

Food		Compound or element (conc. ± SD)						
		BPA	BADGE·2H ₂ O	Fe	Cd	Ni	Cu	Zn
		µg/kg		mg/kg				
Fava beans (brand A)	Unheated	50.53 ± 2.63	141.00 ± 11.60	13.06 ± 0.50	0.02 ± 0.00	0.38 ± 0.01	1.75 ± 0.05	6.99 ± 0.18
	Heated	49.80 ± 11.30	145.24 ± 9.00	12.40 ± 1.90	0.02 ± 0.00	0.29 ± 0.06*	1.84 ± 0.05	7.08 ± 0.07

703 n=3
704 * significant difference in concentration is noticed between heated and unheated cans (p<0.05)



705

706 **Figure 1:** Impact of heat treatment on BPA and BADGE.2H₂O levels in brand A canned food
 707 products (sterilized foods, except pasteurized okra).

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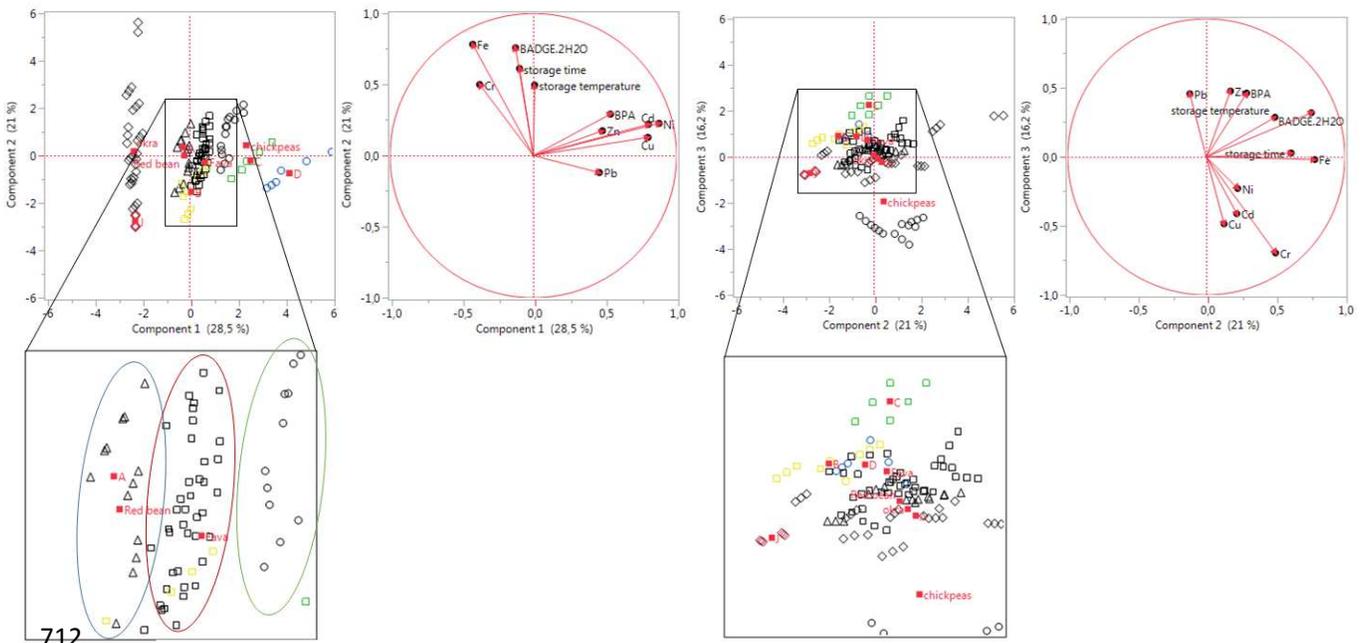
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(a)

(b)

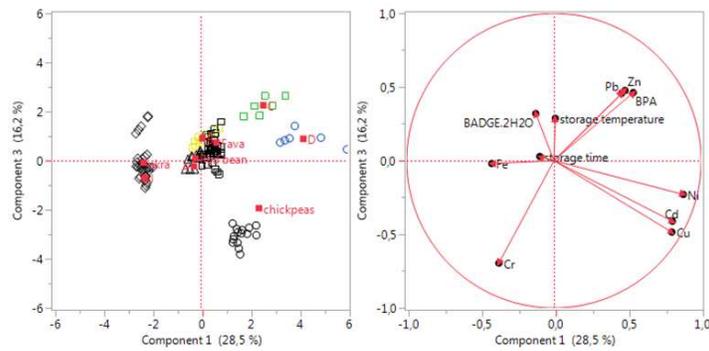


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(c)



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■ Fava beans brand A ■ Fava beans brand B ■ Fava beans brand C ▲ Red beans brand A
 ● Chickpeas brand A ● Chickpeas brand D ◆ Okra cans brand ◆ Okra jars brand A

716

717

718 **Figure 2:** Scores and loadings on the combination of PC1 and PC2 (a), PC2 and PC3 (b), PC1 and PC3 (c)

719 resulting from PCA applied on all our data.

720