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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·2H<sub>2</sub>O 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·H<sub>2</sub>O and/or BADGE·2H<sub>2</sub>O (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·H<sub>2</sub>O 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 6<sup>th</sup> 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 Armariu, 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.2H<sub>2</sub>O (purity grade  $\geq 97\%$ ), BADGE.2HCl  
113 (purity grade  $\geq 95\%$ ), BFDGE (mixture of diastereomers, purity grade  $\geq 95\%$ ), BFDGE.2H<sub>2</sub>O  
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 $\Omega$ , 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 Visiprep<sup>TM</sup> 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<sup>®</sup> -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·2H<sub>2</sub>O  
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·2H<sub>2</sub>O 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·2H<sub>2</sub>O 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/dm<sup>2</sup> for BADGE·2H<sub>2</sub>O,  
314 and 3.9-4.8 µg/dm<sup>2</sup> for BPA. Interestingly, pasteurization had no noticeable effect on BPA  
315 levels (no migration) whereas the highest BADGE·2H<sub>2</sub>O level was observed in pasteurized  
316 canned okra (migration 23.2 µg/dm<sup>2</sup>). 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·2H<sub>2</sub>O 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·2H<sub>2</sub>O 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·2H<sub>2</sub>O, 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·2H<sub>2</sub>O 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·H<sub>2</sub>O 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·2H<sub>2</sub>O 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·2H<sub>2</sub>O level rises from  $119 \pm 25$  µg/kg at day 0 to approximately  
416  $150 \pm 10$  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  $1.6 \pm 0.1$  mg/kg during the 0-493 days'  
426 period increased up to  $2.1 \pm 0.1$  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·2H<sub>2</sub>O 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·2H<sub>2</sub>O, 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·2H<sub>2</sub>O  
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·2H<sub>2</sub>O; (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

523 **7. References**

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656

657

658 **8. Figure captions**

659 **Figure 1:** Impact of heat treatment on BPA and BADGE·2H<sub>2</sub>O 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 <sup>2</sup> )	Free space (cm)	pH <sup>a</sup>	Moisture (%) <sup>b</sup>	Fat (% w/w) <sup>c</sup>	Antioxidants <sup>c</sup>	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 <sup>e</sup> (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 <sup>f</sup>	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 <sup>f</sup>	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 <sup>d</sup>	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 <sup>a</sup> Determined by pH meter, <sup>b</sup> Determined from freeze drying where the difference in mass before and after drying is calculated

668 <sup>c</sup> According to product label, <sup>d</sup> For both cans and jars

669 <sup>e</sup> Ethylene diamine tetraacetic acid, <sup>b</sup> 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 <sub>2</sub> O	Fe	Pb	Cd	Cr	Ni	Cu	Zn
			µg/kg		mg/kg						
Fava beans (brand A)	0*	-	54.60 ± 2.62 <sup>a</sup>	119.37 ± 25.07 <sup>a</sup>	10.73 ± 0.17 <sup>a</sup>	0.03 ± 0.00 <sup>a</sup>	0.01 ± 0.00 <sup>a</sup>	0.12 ± 0.01 <sup>a</sup>	0.3 ± 0.02 <sup>a</sup>	1.62 ± 0.04 <sup>a</sup>	5.83 ± 0.07 <sup>a</sup>
	75 ± 18	22 ± 4	55.81 ± 6.98 <sup>a</sup>	168.87 ± 26.16 <sup>b</sup>	8.79 ± 1.01 <sup>b</sup>	0.03 ± 0.00 <sup>a</sup>	0.01 ± 0.00 <sup>a</sup>	0.14 ± 0.01 <sup>a</sup>	0.31 ± 0.01 <sup>a</sup>	1.55 ± 0.11 <sup>a</sup>	7.32 ± 0.18 <sup>b</sup>
		5 ± 1	46.67 ± 1.68 <sup>b</sup>	154.87 ± 16.41 <sup>b</sup>	10.92 ± 0.25 <sup>a</sup>	0.03 ± 0.00 <sup>a</sup>	0.01 ± 0.00 <sup>a</sup>	0.16 ± 0.00 <sup>b</sup>	0.36 ± 0.00 <sup>a</sup>	1.46 ± 0.10 <sup>a</sup>	7.30 ± 0.17 <sup>b</sup>
	330 ± 24	22 ± 4	48.49 ± 1.50 <sup>b</sup>	152.34 ± 3.20 <sup>b</sup>	10.77 ± 0.19 <sup>a</sup>	0.03 ± 0.00 <sup>a</sup>	0.01 ± 0.00 <sup>a</sup>	0.16 ± 0.00 <sup>b</sup>	0.40 ± 0.01 <sup>b</sup>	1.78 ± 0.16 <sup>a</sup>	7.16 ± 0.28 <sup>b</sup>
		40 ± 2	63.63 ± 9.03 <sup>c</sup>	193.36 ± 5.42 <sup>c</sup>	13.80 ± 0.01 <sup>c</sup>	0.03 ± 0.00 <sup>a</sup>	0.01 ± 0.00 <sup>a</sup>	0.16 ± 0.00 <sup>b</sup>	0.43 ± 0.01 <sup>c</sup>	1.65 ± 0.02 <sup>a</sup>	6.68 ± 0.67 <sup>b</sup>
	493 ± 38	5 ± 1	39.75 ± 2.47 <sup>d</sup>	112.12 ± 13.91 <sup>a</sup>	10.51 ± 0.37 <sup>a</sup>	0.03 ± 0.00 <sup>a</sup>	0.02 ± 0.00 <sup>b</sup>	0.14 ± 0.00 <sup>a</sup>	0.34 ± 0.03 <sup>a</sup>	1.84 ± 0.07 <sup>a</sup>	6.56 ± 0.37 <sup>c</sup>
		22 ± 4	50.53 ± 2.63 <sup>a,b</sup>	141.00 ± 11.60 <sup>a,b</sup>	13.06 ± 0.50 <sup>d</sup>	0.03 ± 0.00 <sup>a</sup>	0.02 ± 0.00 <sup>b</sup>	0.15 ± 0.00 <sup>b</sup>	0.38 ± 0.01 <sup>b</sup>	1.75 ± 0.05 <sup>a</sup>	6.99 ± 0.18 <sup>b,c</sup>
	730	40 ± 2	47.63 ± 1.90 <sup>b</sup>	149.14 ± 14.92 <sup>a,b</sup>	15.33 ± 0.08 <sup>e</sup>	0.03 ± 0.00 <sup>a</sup>	0.02 ± 0.00 <sup>b</sup>	0.15 ± 0.01 <sup>b</sup>	0.38 ± 0.00 <sup>b</sup>	1.86 ± 0.06 <sup>a</sup>	6.72 ± 0.04 <sup>c</sup>
		5 ± 1	NA	NA	10.38 ± 0.16 <sup>a</sup>	0.03 ± 0.00 <sup>a</sup>	0.02 ± 0.00 <sup>b</sup>	0.14 ± 0.02 <sup>a</sup>	0.37 ± 0.02 <sup>b</sup>	2.13 ± 0.07 <sup>b</sup>	6.48 ± 0.10 <sup>c</sup>
	40 ± 2	NA	NA	12.96 ± 0.01 <sup>d</sup>	0.03 ± 0.00 <sup>a</sup>	0.02 ± 0.00 <sup>b</sup>	0.14 ± 0.01 <sup>a</sup>	0.35 ± 0.03 <sup>a</sup>	2.13 ± 0.07 <sup>b</sup>	6.65 ± 0.28 <sup>c</sup>	
40 ± 2	NA	NA	14.74 ± 0.24 <sup>f</sup>	0.03 ± 0.00 <sup>a</sup>	0.02 ± 0.00 <sup>b</sup>	0.16 ± 0.01 <sup>b</sup>	0.38 ± 0.03 <sup>b</sup>	2.04 ± 0.09 <sup>b</sup>	6.89 ± 0.27 <sup>b,c</sup>		
Fava beans (brand B)	0*	-	24.61 ± 3.59 <sup>a</sup>	116.20 ± 19.78 <sup>a</sup>	5.59 ± 0.32 <sup>a</sup>	0.06 ± 0.01 <sup>a</sup>	0.01 ± 0.00 <sup>a</sup>	0.05 ± 0.00 <sup>a</sup>	0.11 ± 0.00 <sup>a</sup>	2.59 ± 0.04 <sup>a</sup>	4.29 ± 0.16 <sup>a</sup>
	75 ± 18	22 ± 4	19.61 ± 4.80 <sup>a</sup>	210.89 ± 15.18 <sup>a</sup>	8.82 ± 0.41 <sup>b</sup>	0.10 ± 0.01 <sup>b</sup>	0.01 ± 0.00 <sup>a</sup>	0.07 ± 0.00 <sup>b</sup>	0.14 ± 0.01 <sup>b</sup>	2.67 ± 0.06 <sup>a</sup>	4.43 ± 0.27 <sup>a</sup>
	493 ± 38	22 ± 4	NA	NA	11.58 ± 0.94 <sup>c</sup>	0.19 ± 0.01 <sup>c</sup>	0.02 ± 0.00 <sup>b</sup>	0.08 ± 0.00 <sup>c</sup>	0.24 ± 0.01 <sup>c</sup>	2.52 ± 0.18 <sup>a</sup>	4.41 ± 0.02 <sup>a</sup>
Fava beans (brand C)	165 ± 15	22 ± 4	104.42 ± 19.20	181.21 ± 16.30	7.44 ± 0.69 <sup>a</sup>	0.15 ± 0.00 <sup>a</sup>	0.02 ± 0.00 <sup>a</sup>	0.08 ± 0.00 <sup>a</sup>	0.41 ± 0.02 <sup>a</sup>	2.60 ± 0.16 <sup>a</sup>	4.34 ± 0.41 <sup>a</sup>
	493 ± 38	22 ± 4	NA	NA	10.16 ± 0.58 <sup>b</sup>	0.21 ± 0.02 <sup>b</sup>	0.03 ± 0.00 <sup>b</sup>	0.08 ± 0.01 <sup>a</sup>	0.50 ± 0.03 <sup>b</sup>	2.75 ± 0.17 <sup>a</sup>	4.41 ± 0.32 <sup>a</sup>

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

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

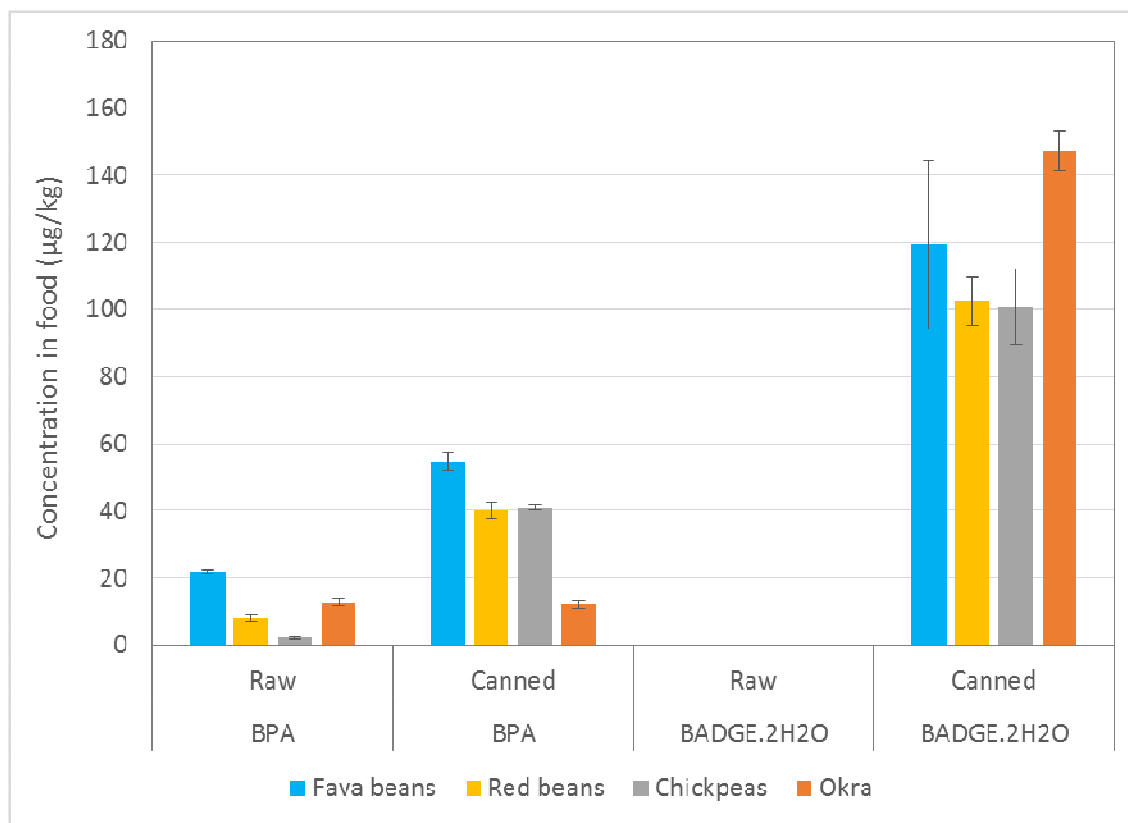
697 n=3  
698 NA: not analyzed, ND: not detected  
699 \* significant difference in concentration is noticed between dented and undamaged cans (p<0.05)

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701  
702

**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. $\pm$ SD)						
		BPA	BADGE·2H <sub>2</sub> O	Fe	Cd	Ni	Cu	Zn
		$\mu\text{g/kg}$		$\text{mg/kg}$				
Fava beans (brand A)	Unheated	50.53 $\pm$ 2.63	141.00 $\pm$ 11.60	13.06 $\pm$ 0.50	0.02 $\pm$ 0.00	0.38 $\pm$ 0.01	1.75 $\pm$ 0.05	6.99 $\pm$ 0.18
	Heated	49.80 $\pm$ 11.30	145.24 $\pm$ 9.00	12.40 $\pm$ 1.90	0.02 $\pm$ 0.00	<b>0.29 <math>\pm</math> 0.06*</b>	1.84 $\pm$ 0.05	7.08 $\pm$ 0.07

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



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

708

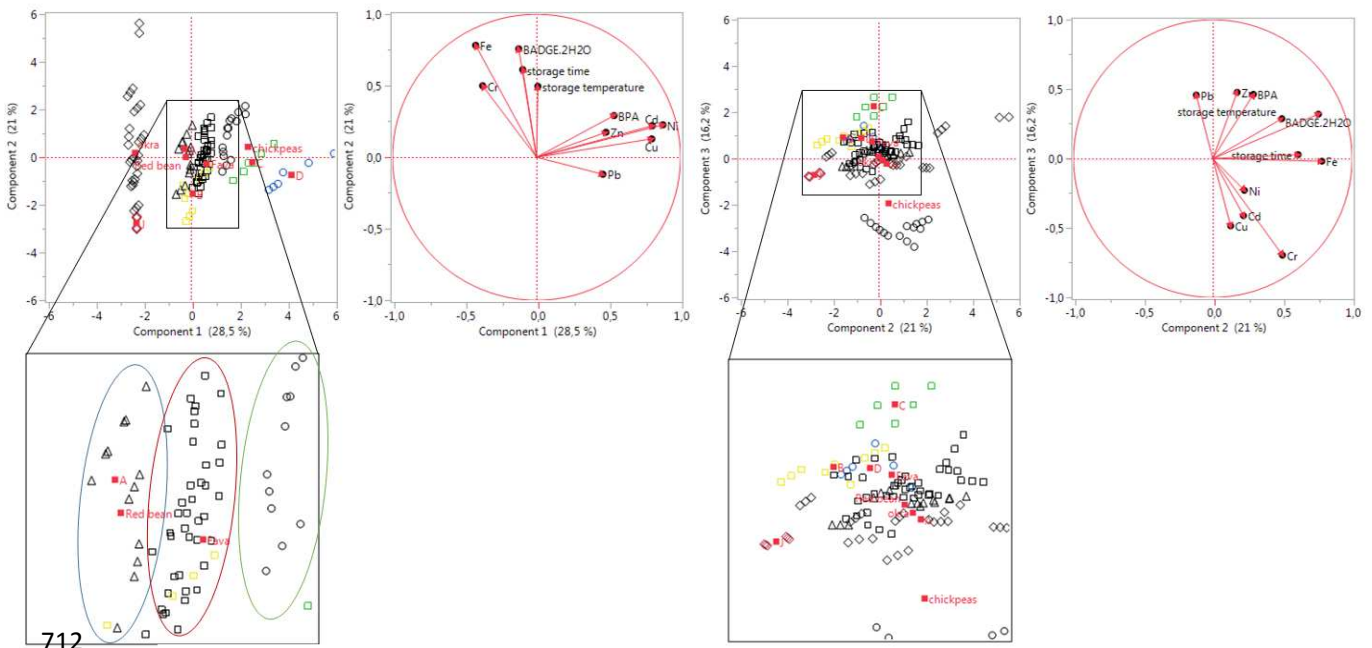
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(a)

(b)

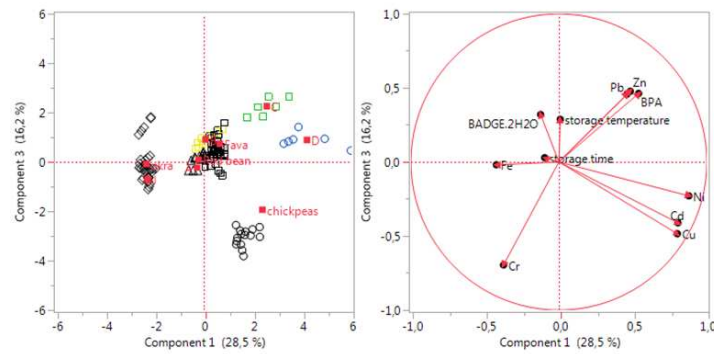


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714

(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