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

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Abstract

For the very first time, this study investigates the simultaneous migration of several metals and bisphenol compounds from coated tinplate cans into vegetable foods highly consumed worldwide. The role played by heat treatment, food type, can brand, storage conditions, can denting and cooking food directly in cans is also assessed. Migration of bisphenol compounds (only BPA and BADGE·$2H_2O$ detected) was mainly affected by sterilization, whereas metal release was greatly influenced by storage. Based on a principal component analysis different migration pattern groups were highlighted: BPA and Zn (and Pb to a lesser extent) showed similar migration trends, with dependence on food type, storage temperature and can brand. Cd, Ni and Cu were similarly influenced by food type and can brand. Fe has a particular trend, with clear influence of storage time, and to a lesser extent of food type. Overall Fe and BADGE·$2H_2O$ migration were favored in acidic food.

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

1. Introduction

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

Several trace metals are prone to migrate, among them tin, iron, lead, cadmium, chromium, nickel, zinc and copper being considered as the most common since they are often used in metal containers. In particular, low levels of tin are currently found in foods and beverages packaged in unlacquered or partially lacquered tinplate cans (Arvanitoyannis and Kotsanopoulos, 2014). Also, iron is the basic element in the steel layer of food cans, while cadmium, nickel and copper may be found as alloying elements in steel. Furthermore, chromium treatment is widely applied to make the tin layer in tinplate cans less susceptible to oxidation damage and to improve the enamel adherence (Arvanitoyannis and Kotsanopoulos, 2014). Cr is also usually used in can lids. Likewise, zinc could be present to enhance tin and steel resistance to corrosion (Cederber et al., 2015). Finally, lead is often found in metal packages, so that it is one of the most important contaminants derived from packaging materials (Petropoulos, Raptopoulou, Pasias, Thomaidis and Proestos, 2018). Accordingly, the resolution of Council of Europe on metals and alloys used in food contact materials and articles has reported the need for specific release limits (SRLs) for several trace metals to limit food contamination (Council of Europe, 2013). In addition, due to their toxicity, Sn, Pb and Cd are routinely determined in foodstuffs under the requirements of the European Regulation n°1881/2006.

Besides trace metals, organic migrants are also of great concern. Common coating materials for food cans are epoxy resins, with possible migration of several bisphenol compounds. Indeed, bisphenol A diglycidyl ether (BADGE) is a key building block of epoxy resins (upon reaction of bisphenol A (BPA) with epichlorhydin). Yet, migration studies from epoxy-phenolic coated cans with aqueous foods or food simulants have shown that the migrant BADGE rapidly undergoes hydrolysis to $BADGE \cdot H_2O$ and/or $BADGE \cdot 2H_2O$ (Wagner et al., 2018). Moreover when BADGE is used as a scavenger for hydrochloric acid or in the presence of salty food, $BADGE \cdot HCl$, $BADGE \cdot HCl \cdot H_2O$ and/or $BADGE \cdot 2HCl$ are formed. Similar derivatives are obtained when bisphenol F diglycidyl ether (BFDGE) is used (being synthesized from bisphenol F (BPF) as an alternative to BPA). Due to their possible endocrine disrupting effects, bisphenol compounds have been regulated with specific migration limits (SMLs) established for plastics and coatings that are intended to come in contact with foods. For example, the SML of BPA was fixed to 600 µg/kg by European regulation (EU) n°10/2011, being recently reduced to 50 µg/kg according to amendment n°2018/213 (with application on September 6th 2018).

Many factors affect the migration from tinplate cans. In previous studies it was proved that there is a strong correlation between storage time and migration of several metals (Buculei, Armariei, Oroian, Gutt, Gaceu & Birca, 2014; Buculei, Gutt, Sonia and Adriana, 2012; Kassouf, Chebib, Lebbos and Ouaini, 2013; Parkar and Rakesh, 2014; Petropoulos et al., 2018). More specifically, there is significant migration of Sn when cans are not coated with plastic film layer (Pasias, Papageorgiou, Thomaidis and Proestos, 2012); in this case high contact temperature seems to accelerate the corrosion of unlacquered cans (Blunden and Wallace, 2003; Parkar and Rakesh, 2014). On the other hand, sterilization was shown to have predominant effect on the migration of bisphenol compounds (Wagner et al., 2018). Other factors, including nature of food [pH (Benitez, Cirillo, Gines and Egli, 2006; Errico et al., 2014; Parkar and Rakesh, 2014), fat content, presence of oxidizing agents and nitrates (Abdel-Rahman, 2015), etc.], type of steel (Blunden & Wallace, 2003), tin coating thickness and surface defects (Benitez et al., 2006), lacquer properties [type (Buculei et al., 2012; Geueke, 2016), thickness (Buculei et al., 2014; Wagner et al., 2018), porosity (Buculei et al., 2014; Wagner et al., 2018), etc.] and volume of headspace (Abdel-Rahman, 2015; Blunden and Wallace, 2003; Parkar and Rakesh, 2014), can significantly affect the migration of metals and/or bisphenol compounds. To our best knowledge, no study has ever combined the analysis of both types of contaminants from tinplate cans, probably due to different analytical methods required. Yet, organic and inorganic contaminants behave differently, so that conditions prevailing to their migration may differ. In addition, bisphenol and trace metals levels in food should be anti-correlated since trace metal migration is prevented by the presence of organic coating that may release bisphenols. Accordingly, the current work highlights the influence of several parameters (heat treatment, storage time and temperature, food content, can denting, brand, packaging and cooking food cans) on the migration of both inorganic (Sn, Fe, Cr, Cd, Pb, Ni, Cu and Zn) and organic contaminants (BPA, BPF, BPS, BADGE and BFDGE as well as their di-hydrolysis and di-chlorinated derivatives) from coated tinplate cans into food products. Several Lebanese vegetable food products, frequently canned and consumed worldwide, have been considered in this work. This work studies for the first time the simultaneous migration of trace metals and bisphenol compounds, enabling to point out common trends.

2. Materials and methods

2.1. Reagents and standards

2.1.1. Analysis of bisphenol compounds

Acetonitrile (ACN) (HPLC plus gradient grade and LC-MS grade), water (LC-MS grade), methanol (LC-MS grade), ethanol (anhydrous absolute), acetic acid (RPE glacial), formic acid (FA) (LC-MS grade) and ammonium formate (LC-MS grade) were obtained from Carlo Erba (France). BPA (purity grade ≥99.9%), BPF (purity grade ≥98%), BPS (purity grade ≥98%), BADGE (purity grade ≥95%), BADGE.2H_2O (purity grade ≥97%), BADGE.2HCl (purity grade ≥95%), BFDGE (mixture of diastereomers, purity grade ≥95%), BFDGE.2H_2O (purity grade ≥95%) and BFDGE.2HCl (total assay of the three isomers, purity grade ≥90%) were all obtained from Sigma Aldrich (France). Ultra-pure Milli-Q water (18.2 MΩ, 25°C) was produced by an Integral 3 water purification system from Millipore®.

2.1.2. Analysis of metal elements

All reagents used were of analytical grade. Individual standard solutions were freshly prepared through dilution of stock solutions with ultrapure water. Solutions of iron, tin, lead and zinc were prepared from 1,000 ± 4 mg/L stock solutions from Fluka Analytical (Buchs, Switzerland), cadmium solutions were from 1,000 mg/L stock solutions from Certipur (Darmstadt, Germany), copper solutions were from 1,000 mg/L stock solutions from Acros Organics (New Jersey, USA), chromium solutions were from 1,000 mg/L stock solutions from Alfa Aesar (Kandel, Germany) and finally nickel was 1,000 ± 10 mg/L stock solutions from HACH (Dusseldorf, Germany). KCl buffer was prepared from 99.5% pure KCl from AnalaR (England) while strontium was purchased from Merck (Darmstadt, Germany) with purity >99%. Microwave digestion was performed with nitric acid (69%; AnalaR, England) and hydrogen peroxide (30-31%; Sigma Aldrich, USA). All glassware was soaked in nitric acid (1%) overnight and then rinsed with ultra-pure water before use**.**

2.2. Processing and storage conditions of food samples

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

Canned products of brand A were analyzed from prior to heat treatment (raw food) up to their shelf life of two years (730 days) after heat treatment. As non-heated cans were directly emptied after canning, the contact time between the food and the can was very short, so that we may consider these can contents as raw foods. Still, as the cans were filled by boiling, we cannot exclude a slight release of contaminants from can coating. Heat treated cans were either sterilized (120°C for 30 min - canned legumes, i.e. fava beans, red beans and chickpeas) or pasteurized (100°C for 20 min - canned okra).

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

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

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

2.3. Sample preparation

Each time a can was opened and emptied for analysis, the aspect of can and its food content was carefully examined by naked eye. Generally, the appearance of food and their cans was normal over the studied time and temperature periods. For regular cans, the only worrying appearance was noticed in canned okra samples stored at 40°C for 730 days, with slight rusting appearing on the can external walls and okra pieces showing darker color. In the case of dented cans, no cracking or flaking of the inner coating was observed; a small corrosion was noticed around the external side seam for dented okra cans at 493 days and beyond.

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

2.3.1. Bisphenol compounds extraction from food

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

2.3.2. Bisphenol compounds extraction from empty tinplate cans

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

2.3.3. Dissolution of trace metals

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

2.4. Analysis of the studied contaminants

2.4.1. Analytical instruments and conditions for bisphenol compounds

A UHPLC Agilent® 1260 Infinity Series system equipped with a multi-wave fluorescence detector was used for quantification of bisphenol compounds. The system was accompanied with an auto-sampler maintained at 10°C; the injected volume was set at 20 µL. Pentafluorophenyl grafted octadecyl silica column (C18-PFP, 150*2.1 mm ID, 2 µm particle size) was used for the separation of analytes at constant temperature of 20°C. The mobile phase, consisting of Milli-Q water (A) and HPLC plus gradient ACN (B), was pumped at a flow rate of 0.3 ml/min with the following binary gradient: 0 min - 43% B, 1 min ramp to 50% B (maintained for 4 min), 2 min ramp to 60% B (maintained for 5 min), 1 min ramp to 100% B (maintained for 2 min) and back to 43% B in 1 min (total duration 16 min). The excitation and emission wavelengths of fluorescence detection were set at 230 nm and 316 nm respectively. Calibration was performed using the classical standard addition approach and external aqueous solutions. The results obtained showed no difference between the two approaches indicating no matrix effect. Accordingly, quantification was performed with external calibrations of integrated peak areas of eight standard solutions in the range 0.5 to 250 µg/L. The instrumental repeatability was ensured through replicate injection of calibration standards: relative standard deviations (%RSDs) ranged from 0.45 to 5% for the inter-day precision tests (n=7), and from 0.15 to 6.2% for the intra-day precision (n=3) tests.

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

2.4.2. Analytical instruments and conditions for trace metals

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

2.5. Method validation

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

In the case of trace metal analysis, white cabbage certified reference material (BCR® -679, Sigma Aldrich, Geel, Belgium) was used to control the accuracy of sample treatment and analysis methods. This reference material contained all targeted elements, except Pb and Sn. Overall, recoveries were in the range 94-111% for all considered trace metals (see **Supplementary material Table S5**). The accuracy of the used method for Pb and Sn was previously confirmed by Kassouf et al. (2013) on chickpeas samples.

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

2.6. Statistics

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

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

3. Results and discussion

In all our samples (raw and canned foods), despite numerous peaks observed after UHPLC-fluorescence analysis (**Supplementary material Figure S1**), only BPA and $BADGE \cdot 2H_2O$ could be confirmed with mass spectrometry, in agreement with previous studies reporting that these two compounds are the most abundant bisphenols in canned food (Sun, Leong, Barlow, Chan and Bloodworth, 2006; Yonekubo, Hayakawa and Sajiki, 2008). Also interestingly, Sn levels remained below detection limit in all our samples, possibly due to the acidic pH working range (3.7-5.9) of our foodstuffs not in favor of Sn dissolution (Benitez et al., 2006), as well as the use of fully lacquered cans (lacquering being expected to decrease Sn release by 99.5%) (Abdel-Rahman, 2015).

3.1. Occurrence of bisphenol compounds and metals in raw food

BPA was present in most raw foods in the range ND-21.7 µg/kg (see **Supplementary material Table S6**), possibly due to food contamination from processing on production line (prior to canning or during can filling) since initial contamination of vegetable food seems rather improbable. On the opposite, $BADGE \cdot 2H_2O$ was not detected as expected.

For trace metals (see **Supplementary material Table S7**), overall levels are within the ranges reported for unprocessed vegetables (Akinyele and Shokunbi, 2015; Cederber et al., 2015; Pan, Wu and Jiang, 2016), except for Cr with slightly higher values than reported for canned legumes (0.01-0.08 mg/kg) (Korfali and Hamdan, 2013). Fava beans and red beans had close concentrations of most metals. Among notable differences, Fe and Cu levels were the lowest in okra, while Ni and Cu levels were the highest in chickpeas.

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

3.2.1. Effect of the canning process on contaminant migration

The sterilization process led to the migration of both BADGE·2H_2O and BPA into food (see **Figure 1**) as already observed (Cabado et al., 2008; Geens et al., 2012; Goodson, Robin, Summerfield and Cooper, 2004). Considering the cans' dimensions and the initial levels in raw foods, migration due to sterilization was around 12.5-14.7 µg/dm^2 for BADGE·2H_2O, and 3.9-4.8 µg/dm^2 for BPA. Interestingly, pasteurization had no noticeable effect on BPA levels (no migration) whereas the highest BADGE·2H_2O level was observed in pasteurized canned okra (migration 23.2 µg/dm^2). In that latter case, migration was more influenced by the food properties rather than heat treatment since okra offers conditions that favor rapid BADGE hydrolysis (low pH (3.7) and high water content (93.8%)). This is confirmed by the high percentage (52-94%) of extractable BADGE·2H_2O recovered in our food products rich in water (>70%) (Leepipatpiboon, Sae-Khow and Jayanta, 2005; Munguia-Lopez and Soto-Valdez, 2001). On the opposite, only part (<30%) of extractable BPA was recovered in our canned food samples, far below previous observations reporting 70-100% BPA extraction during sterilization (Paseiro-Cerrato et al., 2017; Goodson et al., 2004).

Considering trace metals migration (see **Supplementary material Table S6**), the effect of heat treatment was positively significant in some cases only, with moderate increase (up to 17-34%) for Ni, Cu and Zn. Fe levels were most affected for okra (58% increase), despite the mild pasteurization treatment, suggesting that the high acidic nature of this foodstuff plays a major role on increasing Fe content in food during heat treatment (Parkar and Rakesh, 2014).

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

Our BPA levels for canned food from Lebanese market were in the range 12.8-54.6 µg/kg (see **Table 2**, storage time 0**)**, which is within the low values of ranges reported for canned food from Japanese (ND-235.4 µg/kg) or US (2.6-730 µg/kg) markets (Yonekubo et al., 2008; Noonan, Ackerman and Begley, 2011). The highest BPA value was noted in fava beans from brand C, which is the only brand studied here that was fully packed outside Lebanon, where the canning procedure and packaging materials may greatly differ and therefore influence BPA migration. These levels do comply with the European specific migration limit of 50 µg/kg (European Commission Regulation (EC) n°2018/213), except for brand A canned fava beans with a value slightly above. In the same samples, BADGE·$2H_2O$ was in the range 101-146 µg/kg, well within reported range (ND-400 µg/kg) (Yonekubo et al., 2008; Sun et al., 2006) and far below the European specific migration limit of 9,000 µg/kg for the sum of BADGE and its hydrolysis derivatives (European Commission Regulation (EC) n°1895/2005).

Among trace metals, the highest levels were observed for Fe and Zn (see **Supplementary material Table S6**). Mean Fe contents varied between 5.6 and 14.0 mg/kg (see **Table 2**, storage time 0**)**, in agreement with values reported for canned vegetables (Korfali and Hamdan, 2013). Zn levels were lower (2.2-5.8 mg/kg) and compare favorably with values reported in canned vegetables (i.e. 7.42 mg/kg) and canned legumes (i.e. 12.8 mg/kg) (Korfali and Hamdan, 2013; Tuzen and Soylak, 2007). Ni concentrations (0.06-0.54 mg/kg) are also comparable to levels reported for Jordanian marketed canned green beans (Massadeh and Al-Massaedh, 2017). On the opposite, our Cu levels (0.55-4.42 mg/kg) are slightly higher than previously reported for canned vegetables (average of 1.63 mg/kg) (Korfali and Hamdan, 2013). For both Ni and Cu, the highest levels were found in chickpeas and the lowest in okra. Cr was present in all samples in the range 0.05-0.22 mg/kg (see **Table 2**, storage time 0**)**, the lowest values being observed in brand B fava beans, and the highest in brand A chickpeas.

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

3.3. Contaminants levels in canned foods over storage

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

3.3.1. General patterns observed

Several groups can be distinguished based on PCA results. Clearly Cd, Ni and Cu behave the same, with their levels linked to the food type (the highest being observed in chickpeas) and brand. BADGE·$2H_2O$, Fe and Cr may be gathered in another group, even though some discrepancy of their behavior is evident, with clear influence of storage, and to a lesser extent of food type and brand. Then, BPA and Zn show similar pattern, their levels being mainly correlated with food type and brand as well as storage temperature; as a matter of fact, as BPA, Zn can be affected by the coating composition since zinc oxide is often added to the lacquer in order to absorb odorous sulfides liberated during and after heat treatment. Pb migration trend is very similar, but its level is additionally influenced by storage time.

3.3.2. Effect of food category

As discussed previously, the highest BADGE·$2H_2O$ and Fe levels are noted in the case of pasteurized okra for unstored canned foods, due to the specificities of this food category (highly acidic pH and aqueous) that favors release of both contaminants. Similar observation can be drawn upon canned food storage since their levels increase over storage in okra whatever the storage conditions. In fact, okra samples are clearly separated from other food samples on PC1 as shown in **Figure 2**, and the highest increase levels over storage are also noted for BPA and Zn, and to a lesser extent Cr and Ni. For trace metals we may assume that acidic pH favors their dissolution from the can and subsequent release. In the case of BPA, it is probably linked to the mild pasteurization. Part of residual BPA could have remained on the coating after pasteurization and then mass transfer is completed during storage time. Similar results were reported for BPA upon pasteurization of canned jalapeno peppers (Munguia-Lopez and Soto-Valdez, 2001). Accordingly, okra samples exhibited the highest dispersion on PC2 linked to storage conditions.

As expected, pasteurized okra contained in glass jars exhibited lower levels of bisphenols (both BPA and BADGE·H_2O not detected) as well as lower contents of Fe. Hence minimal release of Fe was observed between 90 and 330 days (but Fe level still increased by 25%, probably coming from the lid). So, glass jars appears as a safer packaging with regards to chemical contaminants release.

3.3.3. Effect of storage conditions

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

Contaminants exhibiting fast release followed by stabilization

BADGE·$2H_2O$ is characterized by a rapid migration during the first half of shelf life (0-330 days) for most food products and can types, followed by a stabilization of its concentrations for prolonged durations (330-730 days) according to **Table 2**. As an example, for canned fava beans of brand A, BADGE·$2H_2O$ level rises from 119 ± 25 µg/kg at day 0 to approximately 150 ± 10 µg/kg at 330 days (22°C), remaining constant up to 493 days (22°C). The high quantity of BADGE in the can inner lacquer may favor its rapid hydrolysis and release into our aqueous food products during the first days of storage, while an equilibrium is rapidly reached and as a consequence limits its migration.

Contaminants exhibiting slow-release

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

Contaminants with unclear behavior under our tested conditions

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

Contaminants slightly affected or unaffected

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

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

3.4. Effect of can denting

Damage to the can, in the form of denting, had no appreciable effect on the migration of BPA and BADGE·$2H_2O$ in canned fava beans, which is in agreement with results reported for BPA migration in non-acidic canned food (Goodson et al., 2004). At certain times, elements like Fe, Ni, Cu and Zn showed a slight decrease upon denting (see **Table 3**). This unexpected decrease could be related to antioxidants (such as EDTA) present in fava beans (brand A) that can form strong complexes with metal ions. For acidic okra, we observed a significant release of BADGE·$2H_2O$, Fe, Cu and Cd at both storage durations, probably due to corrosion resulting in can damage (the highest effect was observed on Fe, with release enhanced by 86-90% and subsequent Fe level of 61.9 mg/kg at 730 days). So, undamaged food cans are preferable over dented cans, especially in case of highly acidic food.

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

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

4. Conclusion

This work highlights for the very first time the main factors that influence the simultaneous migration of trace metals and bisphenol compounds from coated tinplate cans into vegetable foods. Sn was undetected in all our samples, which may be attributed to the presence of lacquer as well as unsuitable food pH for its dissolution. All other considered metals were found, with some samples that did not comply with the European regulation, either due to levels being above the maximum values authorized in food (e.g. Pb in canned chickpeas of brand D) or to release being above the SRL value (e.g. Fe in canned okra stored at 40°C beyond 493 days, and in dented okra cans). Among bisphenols, only BPA and BADGE·2H_2O were confirmed in our samples; in a few samples (e.g. brand C fava beans) BPA migration was found to exceed its SML value recently set by the European regulation. Our study confirms that sterilization is the main contributing parameter for the migration of free bisphenol compounds (here release less than 80% of maximum free bisphenol compounds was observed); heat treatment in food glass jars should be preferred, as undetected levels of all bisphenol compounds were found in that case. Our PCA results suggest several trends of migration depending on the contaminants. Interestingly, the primary hypothesis that bisphenols and trace metals levels in food should be anti-correlated is invalid based on these results. Besides, the fact that BPA and Zn (and Pb to a lesser extent) have similar trends is interesting and shown for the first time. This suggests that their migration is affected by can composition and coating. In addition, food pH and water content seem to play a major role in favoring migration. Surprisingly, for non-acidic food, can denting as well as cooking food in cans showed no effect on the migration of inorganic or organic targeted migrants. On the other hand, in case of acidic food (namely okra), several recommendations can be drawn for industries and consumers: (i) to store cans under moderate temperature to limit excessive release of Fe and BADGE·2H_2O; (ii) to discard dented cans since high release of Fe is expected; (iii) to control the purity of metal substrate as well as the polymerization and formulation of polymeric coating, since our results confirm major differences in the packaging quality between brands.

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6. Declaration of interest

None

7. References

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8. Figure captions

Figure 1: Impact of heat treatment on BPA and BADGE·$2H_2O$ levels in brand A canned food products (sterilized foods, except pasteurized okra).

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

9. Appendix A. Supplementary material

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 metasulfite (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

* Vacuum packed, ** United Arab Emirates

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

[c] According to product label, [d] For both cans and jars

[e] Ethylene diamine tetraacetic acid, [b] Determined from lyophilization

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_2O	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}
	330 ± 24	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}
		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$^{b, c}$
		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}
	730	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}
		22 ± 4	NA	NA	12.96 ± 0.01^{d}	0.03 ± 0.00^{a}	0.02 ± 0.00^{b}	0.14 ± 0.01^{a}	0.35 ± 0.03^{a}	2.13 ± 0.07^{b}	6.65 ± 0.28^{c}
		40 ± 2	NA	NA	14.74 ± 0.24^{f}	0.03 ± 0.00^{a}	0.02 ± 0.00^{b}	0.16 ± 0.01^{b}	0.38 ± 0.03^{b}	2.04 ± 0.09^{b}	6.89 ± 0.27^{b,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}	4.29 ± 0.16^{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}
	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}

n=3

* after sterilization or pasteurization

NA: not analyzed

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 ($p>0.05$)

MQL: method quantification limit

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_2O	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}
		40 ± 2	46.03 ± 0.98^{e}	500.21 ± 32.17^{e}	67.76 ± 2.50^{g}	0.06 ± 0.00^{a}	0.01 ± 0.00	0.21 ± 0.01^{c}	0.27 ± 0.02^{d}	0.86± 0.06^{d}	5.37 ± 0.13^{e}
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}

n=3

* after sterilization or pasteurization

NA: not analyzed, ND: not detected

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 ($p>0.05$)

MQL: method quantification limit

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

Food	**Storage time (days)**	**Can aspect**	**Compound or element (conc. ± SD)**								
			BPA	BADGE·$2H_2O$	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***

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

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·$2H_2O$	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

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

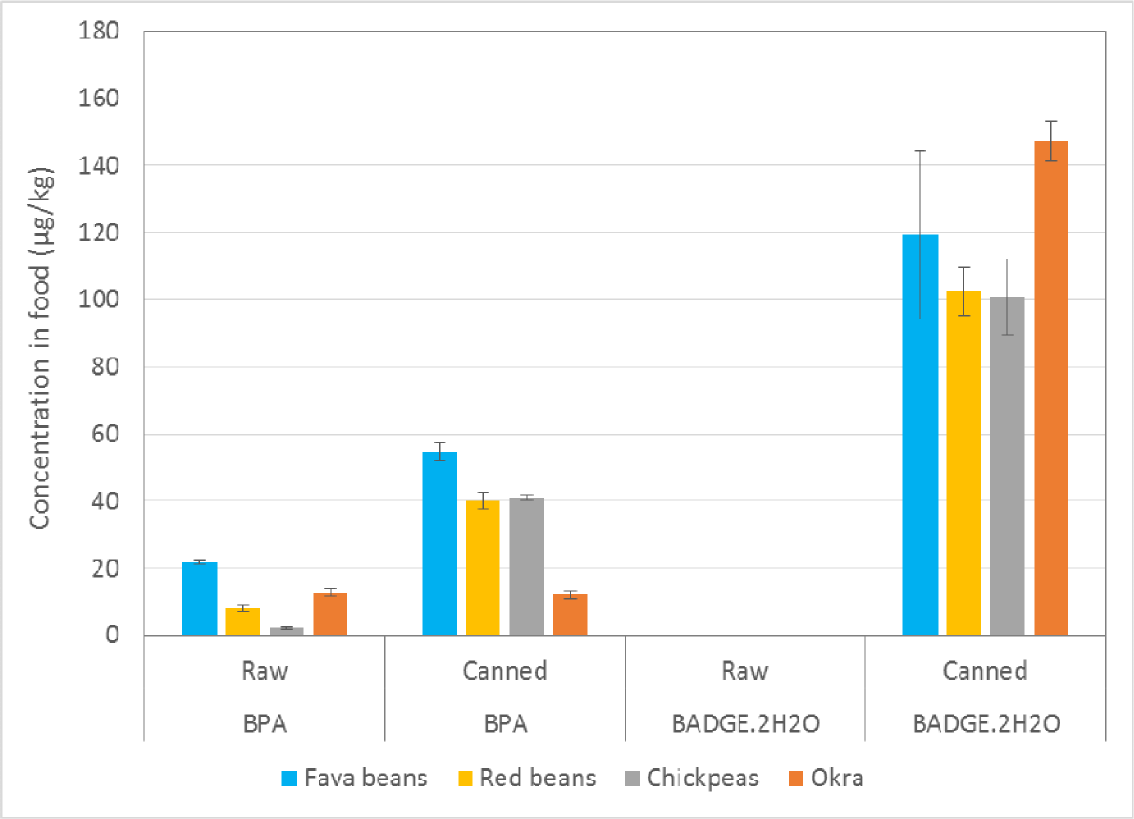

Figure 1: Impact of heat treatment on BPA and BADGE·2H_2O levels in brand A canned food products (sterilized foods, except pasteurized okra).

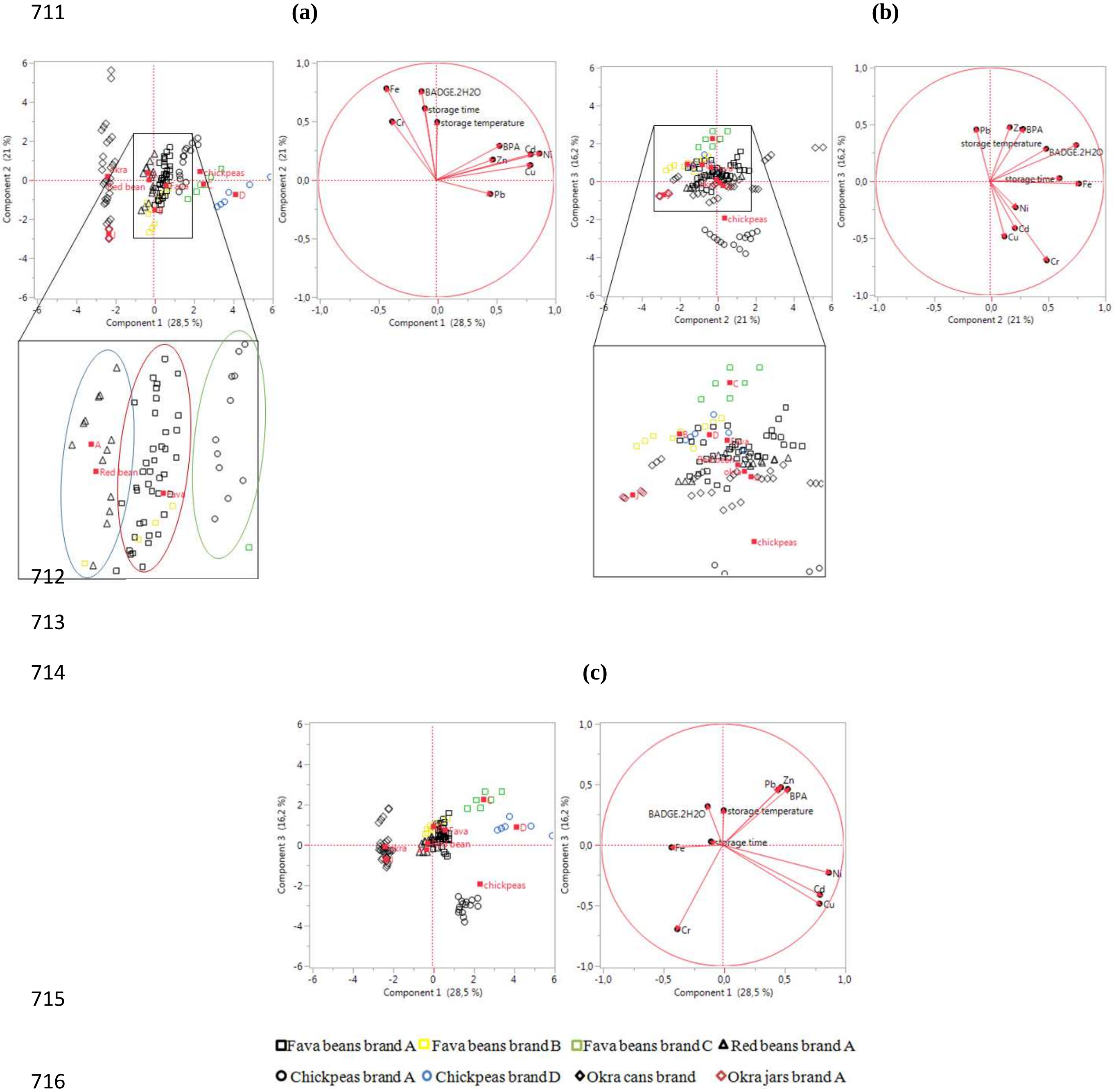

Figure 2: Scores and loadings on the combination of PC1 and PC2 (a), PC2 and PC3 (b), PC1 and PC3 (c) resulting from PCA applied on all our data.