Journal of Food Research; Vol. 2, No. 1; 2013
ISSN 1927-0887 E-ISSN 1927-0895
Published by Canadian Center of Science and Education

Essentail and Toxic Metals in Lebanese Marketed Canned Food: Impact of Metal Cans

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Received: October 16, 2012 Accepted: November 4, 2012 Online Published: January 15, 2013

doi:10.5539/jfr.v2n1p19 URL: http://dx.doi.org/10.5539/jfr.v2n1p19

Abstract

Canned foods are frequently consumed in Lebanon, and limited reported information about metal content in Lebanese marketed canned food. The objective of this study is to assess metal content of different canned food sold in Lebanese market and the impact of metal cans on food quality. Results indicated that Fe has the highest percentage of metals in cans, some cans the % of Al was comparable to Fe and 50% of cans had Sn up to 12%. The analysis of variance (ANOVA) of each metal indicated statistically significant difference of metal levels in the different food categories, except for Cr. In food Fe, Zn, Cu, Al, and Sn levels were below the international permissible levels. But in some artichoke and mushroom Sn levels were close to EU permissible limit, a correlation existed between levels of Sn and Al in cans and the respective food. Lead highest levels were in corn and fava beans, Hg in fish, and both were below PTWI levels. Thirty percent of vegetables and legumes and 45% of fish samples had Cd levels above EU permissible level (0.1 μg/g). This finding necessitates continuous monitoring of Cd levels in canned food for providing citizens with safe food.

Keywords: canned food, can impact, essential and toxic metals, Lebanon

1. Introduction

Canned food are popular food sources all around the world (Mol, 2011), because they are inexpensive and affordable (Storelli, Barone, Cuttone, Giungato, & Garofalo, 2010; Shiber, 2011) such as canned tuna and sardine. For most people, the main route of exposure to toxic elements is through the diet. Food safety is a worldwide major public concern, and the increasing worry about food safety stimulated research regarding the risk associated with the consumption of food contaminated by heavy metals (D'Mello, 2003; Radwan & Salama, 2006). Consequently information concerning dietary intake is of utmost importance in being able to assess risks to human health.

The ingestion of fresh or canned food is an obvious cause to exposure to metals (Ganjavi, Ezzatpanah, Ginvianrad, & Shams, 2010; Nasreddine et al., 2010), not only because many metals are natural components of food stuffs, but also due to environmental contamination and contamination related to food packaging and processing (Ganjavi et al., 2010; Storelli et al., 2010; Mahalakshmi, Balakrishnan, Indira, & Srinivasan, 2012). Trace metals are significant in nutrition either for their essential nature or their toxicity. Iron, copper and zinc are essential micronutrients consumed in adequate amounts to maintain certain physiological functions. But these same essential metals become toxic when consumed excessively (Tuzen & Soylak, 2007a; Nasreddine et al., 2010; Mol, 2011; Mahalakshmi et al., 2012). The recommended daily intake of iron is 10-15 mg/day (Nordiac Council of ministers, 1995) and the provisionally maximum tolerable daily intake PMTDI is 0.8 mg/kg Body weight (JECFA, 1983). While JEFCA (1982) has established for copper a daily requirement of 0.05 mg/kg body weight and PMTDI of 0.5 mg/kg body weight and the daily requirement for zinc to be between 15 and 22 mg/day with PMTDI of 1 mg/kg body weight. In contrast Cd, Pb, and Hg are toxic metals. These metals have been associated with acute and chronic health symptoms (Bakircioglu, Kurtulus, & Ucar, 2011). They are harmful at low concentration and they are not easily biodegradable (Radwan & Salama, 2006; Ganjavi et al., 2010). The provisional maximum tolerable intake of these metals has been constantly reviewed. The provisional tolerable weekly intake (PTWI) for Pb is 25 μg/kg body weight (JEFCA, 2000), for Hg as total inorganic is 4 μg/kg body weight and as methyl mercury is 1.6 μg/kg body weight, and for Cd is 2.5 μg/kg body weight (EFSA, 2009).

Literature has reported extensively the accumulation of Hg in marine food thus contaminating canned marine foods such as tuna and sardine (Khansari, Ghazi-Khansari, & Abdollahi, 2005; Mol, 2011; Shiber, 2011; Ruelas-Inzunza, Patiño-Mejía, Soto-Jiménez, Barbra-Quintero, & Spanopoulos-Hernández, 2011). Also, in Lebanon, a recent study conducted by Obeid et al. (2011) assessed Hg content in fresh and canned fish on the market and reported high levels in some species. Likewise, the accumulation of Pb and Cd in fresh and canned fish has been reported (Khansari et al., 2005; Storelli et al., 2010; Mol, 2011; Shiber, 2011). Furthermore, trace and toxic metals in vegetables have been widely reported in Literature, but limited to canned food. However, accumulation of Hg in mushroom is documented (Tuzene & Soylack, 2007b). A high content of Cd was reported in Lebanese vegetable products. The major sources of the high exposure of the Lebanese population to Cd in their diet are grains and vegetables (Nasreddine et al., 2010; JEFCA, 2011). Yet, there is barely any research regarding toxic metals in canned meat.

Contamination of food by metals is also the result of the manufacturing procedure, the equipments used during the process, packing and storage (Bakircioglu et al., 2011). Food cans are generally tinplate and/or aluminum. Tin plate is low carbon steel coated as sheet on both sides with commercially pure tin. One third of total tin production goes into manufacturing of tin plates for which food packaging is by far the largest consumer of its production (Bludin & Wallace, 2003).The use of tinplate will ultimately result in some tin dissolving in food. Although tin is not a toxic metal, but gastrointestinal perturbation occurs when it is present in concentration above 200 mg/kg (Munteanu, Chirila, Sranciu, & Marin, 2010). According to WHO/FAO committee the maximum inorganic tin in canned food is 250 mg/kg (JEFAC, 2006), but to EC 1881/2006 is 200 mg/kg and the PTWI is 14 mg/kg body weight (EU, 2006). Additionally, other metals like Fe, Cr, Cu and Zn might leach into food especially in non-lacquering steel containers. Aluminum is also widely used in food contact material such as cans and can ends. Exposure to aluminum is usually not harmful (ATSDR, 1997) and it is excreted by the kidneys, and only a minute amount of aluminum is absorbed (JECFA, 1989). However, it leaches into canned food in the presence of acidic media, and the PTWI for Al is 1 mg/kg body weight (JECFA, 2006). Lead might exist in canned food stuff due the leaching from the soldering materials.

Canned food is frequently and largely eaten in Lebanon. In view of the scarcity of information about essential and toxic metal content in Lebanese sold canned food, the objective of this study is to assess the metal content in different canned food types sold on the Lebanese market and the impact of metal can on food quality. Consequently toxic metal levels in canned food will be evaluated for human health concern and for the provision of safe good food quality.

2. Materials and Methods

2.1 Samples

Forty five samples of canned food (fish, meat, poultry, vegetables, and legumes) of different brands and different manufacturing countries were purchased from local supermarkets. The canned foods were put in three categories: 1) fish, 2) Meat and chicken, 3) vegetables and legumes. The canned fish products, all imported, were chosen from 8 different tuna fish brands and 6 different sardine brands. While, the meat (chicken, pork, and beef) were of 11 different brands and of three types (luncheon meat, hot dogs and liver paste), and only 2 brands (chicken) were locally manufactured. The 20 samples of vegetables and legumes consisted of mushroom, corn and artichoke (all imported), fava beans and green beans (imported and locally manufactured), and chicken peas and dried beans (locally manufactured).

2.2 Sample Preparation and Digestion

The cans were opened, the liquid content was drained off within 30 minutes, using plastic sieve (sieve size 2 mm), and then each food sample was homogenized for later digestion and metal analysis. Whereas, the cans and cover were cleaned with hot water and dried for metal scanning.

For the determination of metals in canned food, the following digestion procedure was followed on a replicate of each sample: one gram of each sample was weighed into 150 mL beaker and 50 mL of freshly 1:1 (v:v) H_2O_2 (30%): HNO_3 (65%) was added slowly in portions. Each beaker was covered with a watch glass and stored at room temperature for 48 h. Then, samples were heated on hot plate until the solution was clear. The solution was allowed to cool and sonicated for 5 minutes. The clear solution was filtered into a flask using 0.45 µm pore size under vacuum, then transferred into a 25 mL lidded plastic tube and diluted with deionized water to the mark, inserted in water bath at 60^{o}C for 30 minutes. Finally, 170 µL of phosphoric acid was added as a modifier to each tube and shaken using tube-shaker. The tubes were stored at 4^{o}C.

2.3 Metal Analysis

2.3.1 Cans

The percentage content of each metal in can and lids of different samples were determined using handheld XRF technique. The XRF brand is Niton XL3 GOLLD hand held (Thermo Fisher Scientific) which is energy dispersive x-ray fluorescence (EDXRF) with up to 50 kV x-ray tube source and optimized silicon drift detector (SDD).

2.3.2 Food

The concentration of Cd, Cr, Cu, Fe, Pb, Zn in the prepared and digested food samples were determined using AAS-Graphite furnace ("Shimadzu" AA-6300) and background correction deuterium lamp. Working standard solutions were prepared by dilution of stock solutions (1 mg metal/ml in 2% HNO_3) with MilliQ water. The concentrations of Al, Hg, Sn were determined by ICP-MS (Agilent ICP-MS 7500-Ce, Japan). For the determination of the efficiency and accuracy of digestion procedure, the Certified Reference Material (CRM) was used and included oyster tissue (NIST 1556b) and Tomato leaves (NIST 1573a). Oyster tissues and tomato leaves in triplicates were digested and adjusted similar to samples. Table 1 and Table 2 indicate a good % recovery.

Table 1. Recovery of metals in tomato leaves certified material

Element	Certified value (μg/g)	Our value(μg/g)	Recovery (%)
Al	598±12	575±36	96
As	0.112±0.004	0.106±0.005	94
Cd	1.52±0.04	1.45±0.05	95
Cr	1.99±0.06	1.87±0.17	94
Cu	4.7±0.14	4.8±0.33	102
Fe	368±7	353±25	96
Hg	0.034±0.004	0.031±0.004	94
Zn	30.9±0.7	29.5±0.9	95

Note: The certified tomato leaves is from National Institute of Standards and Technology. Reference number (NIST 1573a).

Table 2. Recovery of metals in oyster tissue certified material

Element	Certified value (μg/g)	Our value(μg/g)	Recovery (%)
Al	197.2±6	195±10	99
As	7.65±0.65	7.32±0.75	95
Cd	2.48±0.08	2.37±0.07	95
Cu	71.6±1.6	69.5±2.7	97
Fe	205.8±6.8	208±8.7	101
Hg	368±7	353±25	96
Pb	0.308±0.009	0.288±0.01	94
Zn	1424±46	1333±0.9	94

Note: The certified oyster tissue is from National Institute of Standards and Technology.Reference number (NIST 1556b).

3. Results and Discussion

3.1 The Mettalic Distribution in Cans

The metallic constituents of cans of the different kinds of food as predicted by XRF analysis are given in Table 3.

The table presents the composition as percentage range of the metal in a particular can of food type, as well as the orign (manufacturing country) of the food. Moreover, the used handheld XRF does not record carbon composition. Thus, the percentage composition is only in terms of metal constituents per total metals content.

The highest percentage of metal in all cans is Fe. In fish product cans, it ranged between 81 and 96 %. Aluminum was found in sardine cans (Table 3), and ranged between 1.5 to 11%. Whereas, tin percentage composition was up to 6.5% in tuna cans and 15.2% in sardine cans. Most probably the type of cans used for fish storage is stainless steel tinplated, and the higher percentage of aluminum in sardines is due to the use of aluminum as can ends. The reported Ti in fish cans (up to 5.3%) is attributed to the lacquer in order to increase the adhesion to can walls or for improving the mechanical strength of the coating (Kontominas, Prodromidis, Paleologos, Badeka, & Georgantalis, 2006). While in meat cans, the percentage range of Fe metal in sausages (hot dogs) was between 85 and 96 %, but in both luncheon meat and liver paste, the percentage of Fe was lower and ranged between 42 and 95%. Yet, those cans with low Fe fraction, contained high percentages of Al, reaching 50%. Thus the luncheon meat and liver paste cans are made of stainless steel and aluminum lacquered inside wall with high percentage of Ti, reaching 11%. With regard to cans used for vegetables and legumes, the metal composition were similar to those used in cans of fish forms. These cans were mainly stainless steel tinplated with a high Fe percentage composition (ranging between 82 and 96%), and Sn ranging between 1.5 to 16%. In some cans (Fava beans), the proportion of Al reached 15% and that of Cr 12%. The high Al percentage is also due to its occurrence in end cans, and Cr in stainless steel. Chromium can reach that high percentage in stainless steel food cans; it serves in passivizing the tinplate surface (EC, 2002).Other metals that are components of metal cans like Cu and Zn had very low composition (not detected - 0.09%).

Table 3. Percentage range composition of metals in cans

Food	Type	Manufacturing Country	% range						
			Fe	Al	Zn	Sn	Cu	Cr	Ti
Fish	Tuna	Thailand Vietnam	85-96	ND	ND-2.5	0.02-6.52	0.02-0.04	0.8-5.7	ND-1.20
	Sardine	Morroco Denmark Thailand	81-92	1.5-11.8	ND-0.04	4.35-15.2	ND-0.04	0.65-1.15	ND-5.3
Meat	Luncheon	Holland, KSA, Lebanon, China	43-95	ND-50	ND-0.09	0.70-1.15	0.02-0.35	0.11-1.24	4.5-11
	Hot Dogs	France, Denmark, Spain	85-96	ND-8	ND	ND-5.2	0.01-0.04	0.5-2.45	ND-0.10
	Liver paste	Spain, France	42-82	7-44	0.08-0.15	ND	0.02-2.06	4.5-5.5	8.5-10.5
Vegetables and legumes	Mushroom	China	80-92	ND-2.5	ND-0.10	2.5-16.5	ND	3-7	2-4
	Artichoke	Peru Egypt	82-95	ND-2.2	ND	10-15	ND	2-4.5	ND-
	Green Beans	France, Lebanon	83-96	ND-3	ND	ND-12	ND	1-5	0.8-1.0
	Corn	China Thailand	83-94	ND-4.5	ND	0.03-7	ND	1-7.5	0.06-5
	Fava Beans	Dubai Lebanon	75-85	9-15	ND	ND-1.5	ND	2-12	ND
	Chicken Peas	Lebanon	82-96	ND-1.2	ND	2.5-13	ND	0.8-2	1.2-5
	Dried Beans	Lebanon	86-96	ND-1	ND	ND-2.0	ND	2-4	ND-10

3.2 Metals in Food

3.2.1 Fe, Zn, Cu

Iron, zinc and copper are considered essential micronutrient, but in high levels they become health hazards. Table 4 present the mean levels and ranges of these metals in the studied food categories (fish, meat, vegetables and legumes); as well as mean levels in respective food type. The analysis of the variance (ANOVA) indicated a significant statistical difference of Fe ($p < 0.001$), Zn ($p < 0.001$), and Cu ($p = 0.021$) content in the food categories.

Table 4. Levels of essential metals (Fe, Zn, and Cu) detected in canned food

Food	Iron (µg/g)		Zinc (µg/g)		Copper (ug/g)	
	Mean±S.D	Range	Mean±S.D	Range	Mean±S.D	Range
Canned fish [a]	13.23±5.21	3-21	8.43±3.14	4-14	0.65±0.42	0.20-1.60
Tuna [b]	12.50±5.5	3-20	6.57±1.84	4-9	0.49±0.21	0.23-0.80
Sardine [b]	14.40±5.07	7-21	11.40±2.41	8-14	0.92±0.56	0.34-1.60
Meat [a]	16.00±5.44	10-25	15.00±4.17	10-22	0.97±0.78	0.50-3.20
Luncheon meat [b]	17.40±5.55	12-25	15.20±5.55	11-22	0.66±0.18	0.50-0.95
Hot dog [b]	12.25±2.87	10-16	12.75±2.92	10-17	0.70±0.21	0.55-1.00
Liver paste [b]	20.00±7.07	15-25	19.50±7.12	17-22	2.30±1.27	1.40-3.20
Vegetable and Legumes [a]	8.25±3.61	4-16	7.42±2.91	2-12	1.63±1.11	0.03-4.00
Vegetables [b]	9.50±4.03	4-16	6.72±2.15	2-10	1.28±0.81	0.37-3.00
Legumes [b]	6.37±1.77	4-10	8.5±3.61	4-13	2.14±1.35	0.03-4.00

[a] Food Category; [b] Food Type.

The highest mean levels of Fe and Zn were detected in canned meat products. The mean content of Fe and Zn in canned meat are respectively 16.00 µg/g and 15 µg/g, with respective ranges between 10 and 25 µg/g, and 10.5 and 22 µg/g. Moreover, among all canned meat products, liver paste contained the highest levels of Fe (25 µg/g) and Zn (22 µg/g) and the lowest in sausages (≈12 µg/g). Literature does not cite reported values of Fe and/or Zn in canned meat products. However, Nasreddine et al. (2010) reported amounts of Fe (44.55 µg/g) and Zn (44 µg/g) in fresh Lebanese meat and poultry. Whereas, the mean level of Fe and Zn in canned fish are respectively 13.23 µg/g and 8.43 µg/g , and respective ranges between 3 and 21 µg/g, and between 4 and 14 µg/g. For both Fe and Zn the levels in canned sardine (14.4 µg/g and 11.4 µg/g) are higher than in canned tuna (12.5 µg/g and 6.5 µg/g). Our reported values of Fe and Zn in canned fish are slightly lower than the reported levels by Tuzen and Sylak (2007a) of canned sardine samples (Fe: 17.4 µg/g, Zn: 7.57 µg/g) and canned tuna (Fe: 14.9 µg/g, Zn: 17.8 µg/g) in Turkish supermarkets. The maximum permitted iron level for canned food is 15 µg/g according to the Turkish Food Codex (Tuzen & Sylak, 2007b). Our canned fish had levels (13.32 µg/g) below the Turkish Codex limit, and the canned meat on the borderline (16 µg/g). While, the mean levels of Fe and Zn in canned vegetables and legumes are respectively 8.25 µg/g and 7.42 µg/g. Iron in canned vegetables (9.5 µg/g) is higher than legumes (6.38 µg/g), but Zn mean level in canned legumes (8.5 µg/g) is higher than in vegetables (6.72 µg/g). Furthermore, our reported Fe level in mushroom (11.75 µg/g), green beans (8 µg/g), and corn (12 µg/g) are below the values reported by Tuzen and Soylak (2007b) in mushroom (79.6 µg/g), green beans (31.3 µg/g), and corn (51.2 µg/g). Also our Zn levels in mushroom (8.5 µg/g), green beans (4 µg/g), and corn (6 µg/g) are lower than those of Tuzen and Soylak (2007b) being respectively 21.9 µg/g, 12.8 µg/g, and 8.5 µg/g, and also lower than those of Radwan and Salma (2006) for fresh green beans (14.7 µg/g).

In contrast, the highest copper levels were in vegetables and legumes with a mean level of 1.6 µg/g and the mean level in legumes (2.14 µg/g) is higher than in vegetables (1.27 µg/g). Besides, high levels were in fava beans (4 µg/g) and in chickpeas (2.7 µg/g) and both brands are manufactured in Lebanon. Our Cu levels in canned vegetables were higher than reported Cu levels by Nasreddine et al. (2010) for fresh Lebanese vegetables (0.5 µg/g). Nevertheless, our reported Cu levels in canned vegetables are lower than those reported by others. Copper level has been reported in the range of 7.6-9.6 µg/g (Tuzen, 2003), 0.2-8.5 µg/g (Ferreira, Gomes, & Chaves, 2005), and Tuzen and Soylak (2007b) reported a level of Cu in mushroom of 4.8 μg/g, in corn 3.5 μg/g, and green beans 7.7 μg/g. These Cu levels are higher than our indicated values respectively 1.42 μg/g, 0.88 μg/g, and 0.53 μg/g. Whereas, the mean levels of Cu in canned meat is 0.79 μg/g with a range between 0.5 and 3.2 μg/g, and highest in liver paste. The lowest Cu levels were in canned fish with a mean value of 0.65 μg/g and a range between 0.23 and 1.6 μg/g. But the mean Cu level in canned sardine (0.91 μg/g) is higher than that in tuna (0.49 μg/g). The Cu reported values in canned fish were also below the MAFF guideline value of 30 μg/g (MAFF, 1995). Also, compared to other works our copper levels are lower than those reported for levels in canned fish samples with a range of 0.01-5.33 μg/g by Ikem and Egiebor (2005), and 2.50 μg/g in canned tuna and 1.96 μg/g in canned sardine by Tuzen and Soylack (2007a).

Based on our reported content of Fe, Zn and Cu in canned food, a hypothetical estimate of dietary intake from the highest values of each food category for each metal was assembled based on the supposition of consuming one can of each per day, as well as the intake per kg of a body weight of 70 kg was estimated. For Fe, the maximum level in the three food categories were 1.8 mg in sardine, 1.2 mg in liver paste, and 3.2 mg in mushrooms, thus the total intake of Fe is 6.2 mg per day, which is below the recommended dietary daily intake of 10-15 mg/day (Nordiac Council of Ministers, 1995). The Fe daily intake per kg body weight would be 0.09 mg indicating a lower iron value than its PMTDI of 0.8 mg/kg bw (JECFA, 1983). Following similar estimation procedures for Zn and Cu, the highest levels for both were found in sardine, liver paste, and chickpeas. The Zn intake was found to be 1.6 mg from sardine, 1.1 mg from liver paste, and 2.4 mg from chickpeas, with a total Zn intake of 5.1 mg per day, a value lower than the daily requirement for zinc of 15 and 22 mg/day (JECFA, 1982). The calculated Zn daily intake per kg body weight would be 0.07mg, which is lower than its PMTDI of 1 mg/kg bw. The Cu intake was 0.145 mg for sardine, 0.160 mg for liver paste, and 0.800 mg chickpeas, with a total of 1.11 mg Cu, a value far below daily intake of 10 mg/day (SCF, 1993), and also daily intake per kg body weight (0.016 mg) is far below its PMTDI (0.5 mg/kg bw).

3.2.2 Cr, Al, Sn

Table 5 presents the mean levels of Cr, Al, and Sn in the different food categories and food types. Analysis of variance (ANOVA) indicated a statistical significant difference of Al and Sn levels ($P < 0.001$), but not for levels of Cr ($P = 0.102$) in the different food categories.

Table 5. Levels of Sn, Al, and Cr detected in canned food

Food	Tin (μg/g)		Aluminum (μg/g)		Chromium (ug/g)	
	Mean±S.D	Range	Mean±S.D	Range	Mean±S.D	Range
Canned fish [a]	0.76±0.17	0.09-2.55	1.79±1.10	0.37-4.10	0.05±0.02	0.01-0.07
Tuna [b]	0.50±0.09	0.09-1.18	0.81±0.34	0.37-1.51	0.05±0.01	0.04-0.07
Sardine [b]	1.09±0.53	0.30-2.55	3.12±0.93	0.55-4.10	0.04±0.02	0.01-0.07
Meat [a]	2.40±1.56	0.37-9.50	2.15±0.51	0.09-7.50	0.05±0.02	0.02-0.07
Luncheon meat [b]	1.08±0.55	0.37-2.99	3.34±0.75	1.50-7.50	0.06±0.01	0.05-0.07
Hot dog [b]	4.25±1.87	1.70-9.50	0.15±0.03	0.09-0.15	0.05±0.01	0.04-0.06
Liver paste [b]	2.00±0.71	1.50-2.50	3.23±0.45	0.95-5.50	0.02±0.01	0.01-0.03
Vegetable and Legumes [a]	44.78±25.38	0.85-179	0.74±0.49	0.06-2.70	0.04±0.02	0.01-0.08
Vegetables [b]	63.50±37.89	0.85-179	0.46±0.29	0.06-1.25	0.05±0.0.02	0.01-0.08
Legumes [b]	16.68±8.81	2.50-40	1.63±0.801	0.07-2.70	0.03±0.01	0.01-0.06

[a] Food Category; [b] Food Type.

The indicated levels (Table 5) of Cr in the three food categories were low and ranged in all food samples between 0.01 and 0.08 μg/g. Research on Cr levels in canned food is limited. Most unprocessed food stuff contains less than 0.1 μg/g (Nordic Council of Ministers, 1995). Consequently, our samples did not reflect contamination by Cr and leaching of Cr from cans. Neveretheless, Ni that is not toxic but it is an allergen, and often present in tsailes steel should have been determined. Cosequently, futher works that relate to steel cans should encompass Ni as a constituent.

The Al mean level mean level in in canned fish is 1.79 μg/g with a range between 0.37 and 4.10 μg/g. The mean levels in sardine (3.12 μg/g) were higher than in tuna (0.81 μg/g). Literature does not report Al levels in Lebanese food and/or canned food. However, our reported Al levels in canned fish samples are higher than those reported by Tuzen and Soylak (2007a) in canned tuna (0.45 μg/g) and sardine (0.98 μg/g); but were comparable with levels reported by Mahalakshmi et al. (2012) in Indian canned tunas (3.16 μg/g). Also they were within a range (0.02 to 5.41 μg/g) reported by Turkmen A., Turkmen M., and Tepe (2005). Whereas, the mean level in canned meat is 2.15 μg/g, with a range between 0.09 and 7.5 μg/g. The highest Al levels was in luncheon meat with a maximum value of 7.5 μg/g, and liver paste of 5.5 μg/g. Literature does not report levels of Al in meat. While, the mean levels in vegetables and legumes is 0.73 μg/g, with a range between 0.06 and 2.7 μg/g with levels in legumes higher than in vegetables. The highest level was in fava beans (2.7 μg/g). Our reported levels in mushrooms (1.25 μg/g) and corn (1.2 μg/g) were lower than those indicated by Tuzen and Soylak (2007b) for mushrooms (2.86 μg/g) and corn (1.73 μg/g). The measured levels of Al in unprocessed foods are less than 0.1 μg/g (ATSDR, 1997); but 71 % of studied samples had levels higher than 0.1 μg/g. These high levels correlated with high levels of Al in cans (Table 3). Therefore, Al in our canned food is due to leaching of Al from the metal can and/or owed to the lacquer, which contains Al based additives (Kontominas et al, 2006). Nevertheless, the permissible daily intake of aluminum for an adult is 60 mg/day. Based on our reported content of Al in canned food, an estimate dietary intake, from the maximum Al values in our food (Sardine: 0.459 mg; Luncheon meat: 1.50 mg, Mushroom: 0.25 mg, Fava beans: 0.540 mg; total 2.75 mg/ day or 19.25 mg/ week), is still in the safe range. The weekly intake will be 0.275 mg/kg bw which is below the maximum provisional weakly intake (PTWI) of 1mg/kg bw (JECFA, 2006).

The mean levels of tin in canned fish and meat were respectively 0.73 μg/g and 2.4 μg/. Sardine had higher levels of Sn (1.1 μg/g) than in tuna (0.5 μg/g), and in canned meat, hot dogs had the highest levels of Sn (4.25 μg/g). Literature does not cite levels of Sn in canned meat products, and are limited for canned fish products. Mol (2011) indicated low levels of Sn in canned anchovy (0.00 - 0.91 μg/g), and canned rainbow (0.000-0.135 μg/g). Our Sn levels in tuna are comparable, but slightly higher in Sardine. In contrast, the mean levels of Sn in vegetables and legumes were high (44.78 μg/g), with a range between 0.850 and 179 μg/g. Moreover, the mean levels of Sn in vegetables (63.51 μg/g) were higher than in legumes (16.69 μg/g). High levels were indicated in artichoke (179 μg/g), in mushroom (145 μg/g), and in green beans (40 μg/g) as indicated in Figure1. All of these cans are stored and preserved in liquid media, which enhanced the leaching of tin from the can. The levels of tin in unprocessed food stuffs is less than 1 μg/g. Higher tin concentrations are found in canned food stuffs, and in unlacquered cans it may exceed 100 μg/g (Codex, 1998). The above mentioned food stuff cans were unlacquered, and the cans had high Sn percentages as indicated by XRF analysis of the can (Table 3). Thus from these findings it is advisivalble that vegetables better to be stored in cans with less amount of Sn, and/or be more cealfuly licquired so as leaching of Sn into food is minimal. But though these cans had high levels of Sn, yet they were below the maximum permitted levels of Sn in canned food (250 μg/g) by WHO (JECFA, 2006), and by EU (2006) level of 200 μg/g. Literature reported in a survey in the UK in 2002 (FSA, 2002) of tin content in 400 samples of canned fruits and vegetables that only 2 samples had Sn concentration higher than the EU set limit of 200 μg/g and the average tin concentration in 234 food samples packed in unlacquered cans was 59 μg/g, comparable to our vegetable cans (63.51 μg/g). Additionally, in a recent study by Munteanu et al. (2010) involving the determination of Sn in canned food, the concentration of Sn in mushroom was reported to be 55 μg/g. An estimate of consuming every day a can with a high Sn content (Artichoke, mushroom, and green beans); the daily intake of Sn would be 91 mg of Sn/day, 637 mg of Sn weekly, and weekly intake per kg body weight of 9.1 mg which is below the PTWI of 14 mg/kg bw.

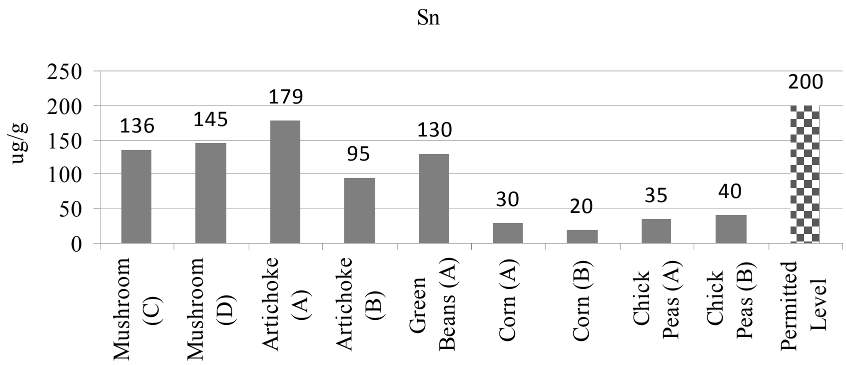

Figure 1. Samples with high levels of Sn

3.2.3 Pb, Cd, Hg

Lead, cadmium and mercury are toxic metals and even in low concentrations they are health hazards since they are not biodegradable. Table 6 presents the mean levels of Pb, Cd, and Hg in the different food categories, and food types. Analysis of variance (ANOVA) indicated statistical significant difference of Pb, Cd, and Hg levels ($P < 0.001$), in the different food categories.

Table 6. Levels of toxic metals (Pb, Cd, and Hg) detected in canned food

Food	Lead (µg/g)		Cadmium (µg/g)		Mercury (ug/g)	
	Mean±S.D	Range	Mean±S.D	Range	Mean±S.D	Range
Canned fish [a]	0.065±0.022	0.007-0.187	0.211±0.083	0.021-0.645	0.146±0.022	0.025-0.395
Tuna [b]	0.062±0.023	0.007-0.187	0.246±0.114	0.026-0.645	0.176±0.035	0.075-0.395
Sardine [b]	0.071±0.030	0.021-0.120	0.156±0.093	0.021-0.525	0.121±0.032	0.049-0.240
Meat [a]	0.007±0.001	0.001-0.032	0.041±0.009	0.025-0.075	0.046-0.024	0.007-0.245
Luncheon meat [b]	0.010±0.001	0.001-0.032	0.054±0.010	0.025-0.075	0.019±0.006	0.008-0.030
Hot dog [b]	0.005±0.001	0.001-0.018	0.029±0.007	0.024-0.040	0.014±0.009	0.007-0.030
Liver paste [b]	0.002±0.001	0.001-0.003	0.030±0.007	0.025-0.035	0.185±0.084	0.125-0.245
Vegetable and Legumes [a]	0.057±0.015	0.001-0.270	0.118±0.065	0.003-0.483	0.058±0.011	0.009-0.155
Vegetables [b]	0.058±0.017	0.001-0.270	0.065±0.029	0.003-0.185	0.057±0.020	0.009-0.155
Legumes [b]	0.056±0.013	0.005-0.270	0.197±0.085	0.075-0.483	0.059±0.018	0.017-0.121

[a] Food Category; [b] Food Type.

The lead levels as indicated by Table 6 were low and its lowest mean is in canned meat and poultry. The mean level of Pb in canned meat is 0.007, with a range between 0.001 and 0.032 µg/g. The lowest lead levels in canned meat were in hot dogs, with a maximum level of 0.018 µg/g, and in luncheon meat and liver paste, the maximum Pb levels were 0.032 µg/g. All of the above indicated levels are below EU (2008) recommended levels of Pb (0.1 µg/g) in fresh meat, no level was set to canned meat, and literature does not cite any work on Pb levels in canned meat. Whereas, the mean level of Pb in canned vegetables and legumes was 0.057 µg/g, with a range between 0.001 and 0.270 µg/g. This high level of Pb was in one brand of canned corn and fava beans, as well as in mushroom the level reached a value of 0.124 µg/g. The Pb levels in corn and fava beans cans are higher than the set EU (2008) maximum permitted levels in vegetables (0.1 µg/g) and legumes (0.2 µg/g), while mushroom was below the set level of 0.3 µg/g. Still, 15 % of the total vegetable and legume cans had higher levels than the set permissible limit. But, the levels of Pb in our canned vegetables were within the range of lead levels reported in fresh vegetables; such as Qin, Zhou, and Qui (2008) reported a value of, 0.240 µg/g, and Wang et al. (2011) a value of 0.286 µg/g. But our levels in legumes (fava bean) are higher than the FAO/WHO study (JECFA, 2011) of lead occurrence in different food categories for European and Asian countries (mean level 0.004 µg/g and a maximum of 0.063 μg/g). In regard to Pb level in canned fish, the Pb mean level is 0.067 μg/g with a range between 0.007 and 0.187 μg/g, and these values of Pb are below the set recommended limit of Pb in fish of 0.3 μg/g (EU, 2006; CODEX, 2008). Moreover, our levels were either below or within the range of Pb reported in other works. Such as a range of 0.015-0.076 μg/g (Khansari et al., 2005) in canned tuna, 0.076-0.314 μg/g in canned fish (Celik & Oehlenschlager, 2007), 0.06-0.27 μg/g in caned sardine (Shiber, 2011), 0.218-0.441 μg/g in Iranian tuna fish (Ganjavi et al., 2010), 0.089 μg/g in Indian canned tuna (Mahalakshmi et al., 2012), and 0.10 μg/g in canned tuna and 0.09 μg/g in sardine (Tuzen & Soylak, 2007a). An estimated weekly consumption of one can with a high Pb content (Corn: 13.5 μg , mushroom: 24.8 μg, fava beans: 54 μg, tuna: 37.4 μg, and sardine: 10.8 μg); the weekly intake of Pb would be 141 μg , and the weekly intake per kg body weight of 2.0 μg which is far below the PTWI of 25 μg/kg bw (EFSA, 2009).

The lowest mean levels of Cd were in meat (similar to Pb) with a mean level of 0.04 μg/g and ranged between 0.025 and 0.075 μg/g. The levels of Cd in canned meat were not recorded in literature for comparison. While, the mean level of Cd in vegetables and legumes is 0.118 μg/g, and levels ranged between 0.003 and 0.438 μg/g. The levels in legumes (mean-0.197 μg/g) were higher than in vegetables (mean-0.065 μg/g). The high levels (Figure 2) were in canned fava beans (mean-0.300 μg/g), and in green beans (0.135 μg/g), and both manufactured in Lebanon, and a level in mushroom in one brand (0.185 μg/g), but manufactured in China. These levels in fava and green beans were higher than the maximum permitted levels (0.1 μg/g) of European Council (EU, 2008); and 31 % of our samples had levels above 0.1 μg/g. The high levels in canned vegetables and legumes manufactured in Lebanon are mostly due to the excess use of phosphate fertilizers in agricultural zones (Bekaa Valley). Our reported values of Cd in vegetables and legumes are higher and/or within those of the reviewed study of Cd occurrence by WHO/FAO in different food categories for European and Asian countries, the range level of Cd in vegetables is 0.006-0.100 μg/g, and in dried vegetables, a range of 0.09-1.0 μg/g (JECFA, 2011). Whereas, the highest Cd levels were indicated in canned fish, with a mean value of 0.211 μg/g, and a range between 0.021-0.645 μg/g. The mean levels in tuna (0.246 μg/g) were higher than those in sardine (0.156 μg/g). Our mean values of Cd in canned fish are above the permitted maximum level in fish (0.1 μg/g) set by EU (2008), and 45 % of our canned fish samples were above 0.1 μg/g, and these are presented in Figure 2. Consequently a continuous monitoring should be conducted for canned tuna and sardine sold in Lebanese market. Literature cites extensively the occurrence of Cd in fish species, and canned fish and sardine; and our Cd levels were within the range and/or higher. For example in canned tuna, a range of 0.025 - 0.494 μg/g (Celik & Oehlenschlager, 2007), and a mean of 0.025 μg/g in Indian tuna (Mahalakshmi et al., 2012); in canned sardine, a range of 0.10-0.69 μg/g (Ashraf, 2006), a mean of 0.19 μg/g (Tuzen & Soylak, 2007a), and a range 0.01-0.07 μg/g (Shibre, 2011). Furthermore, an estimate of a weekly consumption of one can of each food with a high Cd content (tuna: 129 μg, sardine: 47.25 μg, green beans: 27 μg, mushroom: 37 μg, and fava beans: 96.6 μg); resulted in a weekly intake of 337 μg Cd , and a weekly intake per kg body weight of 4.8 μg which is about 2 times the PTWI of 2.5 μ/kg bw (EFSA, 2009).Nevertheless, the probability of choosing these types of canned food is low, and further study should be conducted on the weekly intake of Cd from canned food.

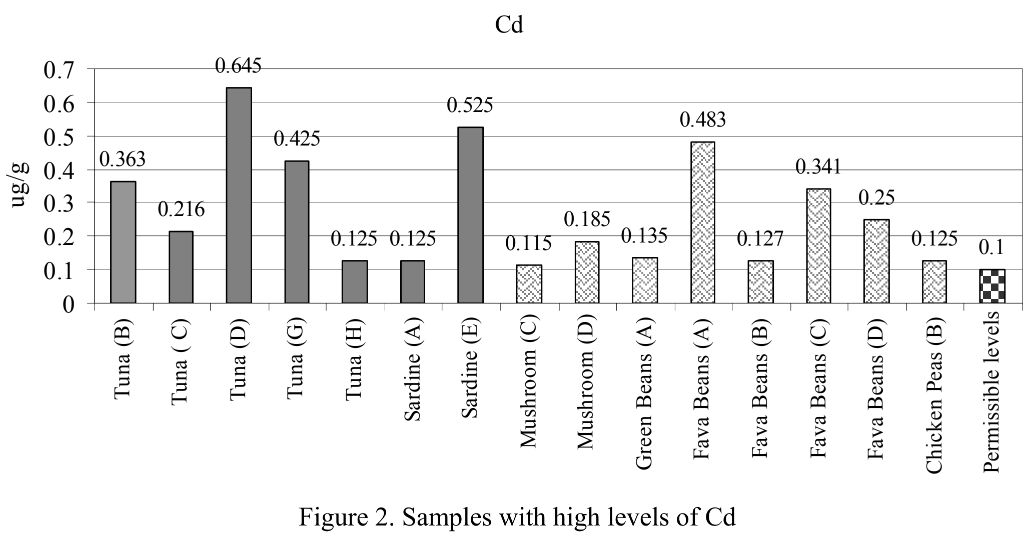

Figure 2. Samples with high levels of Cd

Mercury, also, had its lowest level of Hg in canned meat, whereas in vegetables and legumes it is slightly higher. The mean Hg level in meat is 0.045 µg/g with a range between 0.007 and 0.245 µg/g. Furthermore, in canned meat, liver paste had higher levels compared to luncheon meat and hot dogs. The mean value of Hg in liver paste is 0.185 µg/g, with a range between 0.125 and 0.245 µg/g. Similar to other studied metals, the levels of Hg in canned meat are not mentioned in literature, and limited in fresh meat and poultry. Whereas the mean level of Hg in vegetable and legumes is 0.058 µg/g, with a range between 0.009 and 0.155 µg/g. In addition, the highest vegetable Hg levels were in mushroom (0.155 µg/g), and in fava beans (0.121 µg/g). But, our reported Hg levels in mushroom are lower than those of Melgar, Alonso, and García (2009) for fresh mushroom species (0.480 µg/g), and higher than those of Falandysz et al. (2012) with the highest mean content of Hg (0.046 µg/g). Still our mean levels in vegetables were nearly comparable to the Hg level in fresh vegetables with a mean level of 0.034 µg/g (Wang et al., 2012). With regard to our canned fish samples, they showed the highest Hg levels among studied food categories. The mean Hg level is 0.146 µg/g, with a range between 0.025 and 0.395 µg/g, and a maximum level in tuna (0.395 µg/g) and is higher than in sardine (0.240 µg/g). Nevertheless, the indicated levels in canned fish are below the maximum limit of this metal in fish as 0.5 µg/g (EU, 2006). Furthermore, the mercury levels in fish and canned fish had been extensively reported in Literature. Good agreements were, generally, observed when our results are compared with those reported by others. The mercury range level in tuna is 0.043-0.253 µg/g (Khansari et al., 2005), 0.04-1.79 µg/g (Storelli et al., 2010), 0.25-0.41 µg/g (Ruelas-Inzunza et al, 2011), 0.62 µg/g (Mahalakshmi et al., 2012); and in sardine, 0.2 µg/g (Ikem & Egiebor, 2005) and < 0.009 µg/g (Shiber, 2011). However, our ranges of Hg in canned tuna and sardine sold in Lebanese supermarket of this study are higher than recent reported values in the work done in Lebanon by Obeid et al (2011) with ranges in tuna (0.074-0.119 µg/g) and sardine (0.031-0.061 µg/g), but our canned fish brands are different from those studied by Obeid et al. Furthermore, a weekly consumption of one can of food with a high Hg content (tuna: 79 µg, sardine: 21.6 µg, liver paste: 12.25 µg, mushroom: 31 µg, and fava beans: 24.2 µg); would result in a weekly intake of Hg of 168 µg, and weekly intake per kg body weight of 2.4 which is below the PTWI of 4.0 µ/kg bw (JECFA, 2011)

4. Conclusion

This study has assessed the metal content (essential and toxic) in different canned food categories and brands sold in Lebanese market and the impact of metal cans on food quality. The analysis of variance (ANOVA) indicated statistical significant differences in each metal level in the three canned food categories (fish, meat, vegetables and legumes), except for Cr metal. The essential metals (Fe, Zn, and Cu) daily intake were below the recommended dietary levels and even below the international provisional maximum tolerable level per day (PMTDI). Also Al and Sn daily intake were below the PTWI, but in some cans (vegetables and legumes); the Sn levels were high, approaching the EU Sn permissible limit. Furthermore, the study indicated the leaching of Al and Sn from metal cans into food by the correlation of Sn and Al levels in cans (XRF scanning) and levels in digested food. For the toxic metals, Pb, Hg, Cd, the Pb and Hg levels in canned food were below the international permissible levels and below the PTWI values. Whereas, 31 % of canned vegetables and legumes samples, and 45% of canned fish samples had Cd levels above the EU permissible level. This finding necessitates continuous monitoring of Cd levels in canned food for citizen's provision of safe food. Furthermore, for canned food manufactured in Lebanon, the high Cd may be reduced by more careful handling practices and processing of raw material. A better selection of the fresh material, including an analysis for toxic elements prior to processing, could surely improve the situation. As well as government control on the use of phosphate fertilizers by Lebanese farmers.

Acknowledgements

Mr. Marwan Wehbeh, Chemistry Laboratory supervisor at Lebanese American University, for assisting in metal determination; and Mr. Youssef Korfali for editing the manuscript.

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