#### ARTICLE



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# Cadmium, lead, tin, total mercury, and methylmercury in canned tuna commercialised in São Paulo, Brazil

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#### ABSTRACT

The objective of this work was to determine levels of inorganic contaminants in 30 samples of five commercial brands of canned tuna, acquired on the local market in Campinas, São Paulo, Brazil, in the year of 2015. Total mercury and methylmercury (MeHg+) were determined by atomic absorption with thermal decomposition and amalgamation; and cadmium, lead, and tin were determined by inductively coupled plasma optical emission spectrometry. Results indicated that 20% of the tuna samples surpassed limits determined by the Brazilian and European Commission legislation for cadmium; for lead, the maximum value found was 59  $\mu$ g kg<sup>-1</sup> and tin was not detected in any samples. The maximum values found for total Hg and MeHg+ were 261 and 258  $\mu$ g kg<sup>-1</sup>, respectively. As from the results obtained, it was estimated that the consumption of four cans per week (540 g) of tuna canned in water could surpass the provisional tolerable monthly intake for MeHg<sup>+</sup> by 100%.

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KEYWORDS canned tuna; methylmercury; mercury; cadmium; tin; lead; estimate of ingestion; risk of exposure

# Introduction

Fish has been recognised as an essential food for a balanced diet, providing high quality proteins, vitamins, and a variety of other nutrients of great nutritional importance (Pieniak et al. 2010). In addition, it is a significant source of polyunsaturated fatty acids such as omega 3, whose benefits are related to a decreased risk of cardiovascular diseases and the contribution to normal neurological development in children (Mozaffarian 2009; Swanson et al. 2012).

Fish can be preserved in many ways, including freezing, salting, smoking, and drying, preservation in the form of a canned conserve being currently one of the most used methods (Jedrychowski et al. 2007). In contrast to their potential health benefits, fish-based products have been a constant target of studies since they are considered to be a source of inorganic contaminants such as Hg, Cd, and Pb (Hernández et al. 2010). The disposal of industrial effluents, atmospheric deposition, and accidental spills of toxic chemical products represent sources of pollution in the aquatic environment (Domingo et al. 2007). The contamination of waterbodies by metals is less visible than other types of contamination, but results in an extensive and direct influence on the marine ecosystem and on man (Emami Khansari et al. 2005). The presence of metals in the aquatic environment deserves significant attention

due to their toxicity and the property of accumulating in marine organisms, as well as their persistence in the environment, not being easily degraded in nature (Dórea et al. 2007).

The inorganic form of mercury is biologically transformed into methylmercury (MeHg<sup>+</sup>) by methylating bacteria in aquatic environments, and can be bioaccumulated as it passes along the trophic chain (Carrasco & Vassileva 2014). The fish absorb the MeHg<sup>+</sup> from the water through their gills and by feeding on other aguatic organisms, binding strongly to the proteins that constitute the fish tissues and muscles. The process of cooking does not reduce the MeHg<sup>+</sup> content of fish to any significant degree, and hence consumers adept to fish-based diets are more exposed to the adverse effects of MeHg<sup>+</sup>, principally the neurotoxic effects. This is a particularly relevant question when considering the ingestion of fish by children, pregnant and breastfeeding women, and consumers belonging to the group at risk according to the classification of the Codex Committee for Contaminated Food (Ramón et al. 2008; CAC 2015).

Although studies can be found in the literature reporting on the determination of total Hg (total mercury) in canned tuna, few studies have approached the determination of its organic fraction (methylmercury). The analytical methods mostly used for the determination of MeHg<sup>+</sup> use the techniques of liquid or gas

chromatography coupled to highly sensitive and selective detectors such as atomic absorption spectrometry (AAS) (Jagtap et al. 2011), atomic fluorescence spectrometry (AFS) (Ohki et al. 2013), atomic emission spectrometry, and inductively coupled plasma mass spectrometry (ICP-MS) (Tu et al. 2000). In recent years, the use of thermal decomposition and amalgamation atomic absorption spectrometry (TDA AAS) has been growing in the study of total (Morgano et al. 2015) and organic (Paiva et al. 2016) Hg in food. For the determination of cadmium (Cd) and tin (Sn) in fish, inductively coupled plasma atomic emission spectrometry (Clemens et al., 2011), ICP-MS (Dai et al. 2012), flame atomic absorption spectrometry (Okyere et al. 2015), and graphite furnace atomic absorption spectrometry (Andayesh et al., 2015) have all been used.

The consumption of canned tuna is frequent in Brazil, but there are few studies that evaluate the MeHg<sup>+</sup>, total Hg, Cd, Pb, and Sn contents of this food. Thus, the objective of the present study was to determine the concentrations of these contaminants in samples of canned tuna available on the market in Campinas, Brazil. Total Hg and MeHg<sup>+</sup> were determined by TDA AAS, whereas Cd, Pb, and Sn were determined using inductively coupled plasma optical emission spectrometry (ICP-OES). The results of this study allowed for the evaluation of the ingestion of inorganic contaminants from the consumption of canned tuna in Brazil, and its relationship with the maximum limits (MLs) established by Brazilian and international legislation.

# **Material and methods**

#### Samples

During the year of 2015, three batches of canned tuna from each of five different brands, conserved in both water and oil, were acquired, giving a total of 30 samples. The five brands of canned tuna were the most commonly consumed and available in the largest markets located in the region of Campinas (São Paulo state, Brazil).

After separating from the water or oil, the tuna samples were ground individually using a domestic processer until a homogenous mass was obtained, and these homogenised samples were stored frozen (-18°C) until analysed. The inorganic contaminants were determined in all samples in triplicate analysis.

# **Reagents and standards**

All the reagents used in this study were of analytical grade or above. The water (18.2 M $\Omega$  cm) was purified using reverse osmosis (Gehaka, São Paulo, Brazil) and

the nitric acid in a sub-boiling distiller (Berghof, Eningen, Germany). Toluene p.a. (Synth, Diadema, São Paulo, Brazil) and 30% HCl (Merck, Darmstadt, Germany) were used to extract the organic Hg (methylmercury). A 2.5% (m/v) solution of L-cysteine (Sigma-Aldrich, Steinheim, Germany) was used to stabilise the organic Hg species. Distilled HNO<sub>3</sub> and 30% H<sub>2</sub>O<sub>2</sub> (Merck) were used to digest the samples in order to determine the metals. The analytical curves were prepared as from standard certified solutions of: 1000 mg L<sup>-1</sup> Hg (Fluka, Sigma-Aldrich, Buchs, Switzerland) in 0.5% HNO<sub>3</sub> (v/v); and Cd, Pb, and Sn as from 1000 mg L<sup>-1</sup> solutions (Merck) in 2.5% HNO<sub>3</sub> (v/v).

#### Instrumentation

The digestion and extraction processes of the methylmercury were carried out using a closed microwave system (Start E, Milestone, Sorisole, Italy) equipped with 24 medium pressure Teflon flasks (perfluoroalkoxy alkane, PFA).

The total mercury and methylmercury contents were quantified using the TDA AAS system with a direct mercury analyser (DMA-80, Dual Cell, Milestone).

The inorganic contaminants were determined using ICP-OES, model 5100 VDV (Agilent Technologies, Tokyo, Japan) equipped with a double-pass nebulization camera and a sea-spray nebuliser. Liquid argon of 99.996% purity (Air Liquide, São Paulo, Brazil) was used in the determination of Cd, Pb, and Sn in order to generate the plasma, as both the nebulising gas and the auxiliary gas. Following were the optimised operational conditions of the equipment: power of the radiofrequency generator (1200 W); flow rate of the nebuliser argon (0.5 L min<sup>-1</sup>); main argon flow rate (1 L min<sup>-1</sup> air); auxiliary argon flow rate (1 L min<sup>-1</sup> air); sample flow rate (0.5 L min<sup>-1</sup>), axial mode of vision; number of replicates (n = 3); and the following wavelengths: Cd (214.439 nm), Pb (220.353 nm), and Sn (189.925 nm).

# Microwave-assisted closed digestion system to determine Cd, Pb, and Sn by ICP-OES

A closed microwave digestion system (Start D, Milestone) was used to determine Cd, Pb, and Sn as follows: 1 g of sample was weighed into a polytetra-fluoroethylene digestion flask and 4 mL concentrated HNO<sub>3</sub> plus 4 mL deionised water added and left overnight, after which 2 mL  $H_2O_2$  were added. The flasks were then sealed, transferred to a microwave digester, and the samples digested using four heating ramps as follows, with the application of 1000 W of power: (1) room temperature to 70°C in 5 min; (2) from 70°C to

120°C in 5 min; (3) from 120°C to 170°C in 5 min; and (4) maintain at 170°C for 25 min. After cooling, the flasks were opened and the resulting solution transferred to a 25-mL Falcon tube in 5% (v/v) HNO<sub>3</sub>. The metals Cd, Pb, and Sn were determined by ICP-OES using the external calibration method, the analytical curves being prepared in the following concentration ranges: from 0.002 to 0.5 mg L<sup>-1</sup> for Cd and Pb; and from 0.05 to 10 mg L<sup>-1</sup> for Sn.

# Determination of total mercury

The instrumental conditions used to determine total mercury by TDA AAS were established based on a study carried out by Morgano et al. (2015): the homogenised samples were weighed in nickel recipients (60 and 80 mg for the samples conserved in water and oil, respectively); the drying temperature was 200°C for 60 s; the decomposition temperature was 600°C for 180 s, the desorption temperature was 850°C, and detection was at a wavelength of 253.7 nm.

# Determination of methylmercury (MeHg<sup>+</sup>): extraction with toluene in closed microwaveassisted system

A closed microwave-assisted system was used as described by Paiva et al. (2016). Briefly, the method was as follows: 1 g of sample was weighed into a Teflon PFA recipient followed by the addition of 8 mL toluene, 1 mL of purified water, and 0.75 mL of a 30% (v/v) HCl solution. The analytical conditions of the microwave extractor were as follows: power applied 1000 W; heating ramps of (1) room temperature to 110°C in 10 min; and (2) maintain temperature at 110° C for 5 min. After the extraction, a 4 mL aliquot of the organic phase was removed and transferred to a centrifuge tube containing 2 mL of a 2.5% (m/v) solution of L-cysteine and centrifuged for 6 min at 3500 rpm. A 100 mg portion of the L-cysteine phase containing the organic mercury was weighed into a quartz recipient and the mercury content determined using the DMA-80. The organic mercury content obtained was considered to be composed exclusively of methylmercury. The optimised instrumental conditions for the determination of methylmercury were as follows: sample drying temperature = 120°C for 60 s; decomposition temperature of 300°C for 180 s; desorption temperature of 850° C for 12 s, and wavelength of 253.7 nm. The concentration ranges for Hg detection for the two cells of the equipment were from 0.5 to 20  $\mu$ g kg<sup>-1</sup> and from 20 to 1000  $\mu g kg^{-1}$ .

# Statistical analysis

The results were expressed as the means and the concentration interval analysed by the analysis of variance (ANOVA) and by Tukey's test to verify any significant difference between the means, with a significance level of 95% (p < 0.05), using the XLSTAT programme version 2012.6.03 (Addinsoft, Paris, France).

# **Quality control**

The analytical methods were validated, the exactness and precision of the figures determined, and the linearity of the analytical curves and detection and quantification limits evaluated, all according to INMETRO (2011). The limits of detection (LOD) and quantification (LOQ) were calculated as 3 and 10 times the standard deviation of 10 analytical blanks and multiplying by the dilution factor used for sample preparation (1 g of sample per 25 mL). The exactness of the method was performed in triplicate to determine Cd, Pb, and Sn using certified reference material (NCR TORT-2 - hepatopancreas) from National Research Council of Canada (NRC, Ottawa, ON, Canada), whereas total Hg and methylmercury used oyster tissue (NIST SRM 1566b) from the US National Institute of Standards and Technology (NIST, Gaithersburg, MD, USA) and fish protein DORM-4 from NRC (Table 1). The triplicate measurements averaged 3.76% relative standard deviation (RSD), varying from 5.61% to 1.9% RSD for NCR TORT-2 hepatopancreas; NIST SRM 1566b oyster tissue averaged 2.38% RSD, varying from 5.78% to 2.41% RSD; and NCR DORM-4 fish protein averaged 0.84% RSD, varying from 0.87% to 0.80% RSD.

The precision of the method was evaluated using 16 analytical repetitions from a water conserved canned tuna sample (eight repetitions per day) with variation

**Table 1.** Obtained results for validation of Cd, Pb, total Hg, and MeHg<sup>+</sup> using certified reference materials (CRM).

	Inorganic contaminants							
	Cadmium		Total Hg					
Parameters	(Cd)	Lead (Pb)	(tHg)	MeHg <sup>+</sup>				
Certified values (mg kg <sup>-1</sup> )	26.7 ± 0.6	0.35 ± 0.13	0.27 ± 0.06	0.152 ± 0.001				
Values obtained (mg kg <sup>-1</sup> )	23.2 ± 0.1	0.31 ± 0.03	0.25 ± 0.01	0.168 ± 0.003				
Recovery (%) <sup>a</sup>	87 ± 1	87 ± 2	97 ± 1	111 ± 2				
LOD (µg kg <sup>-1</sup> ) <sup>b</sup>	8.5	30	0.5	1.4				
LOQ (µg kg <sup>-1</sup> ) <sup>c</sup>	28	102	1.6	5.7				
Precision (%) <sup>d</sup>	3.7	4.1	5.5	9.0				

<sup>a</sup>Recovery, n = 3.

<sup>b</sup>LOD (3 s) = detection limit, n = 10.

<sup>c</sup>LOQ (10 s) = quantification limit, n = 10.

<sup>d</sup>Precision = standard deviation (n = 16).

CRM for Cd and Pb = hepatopancreas (TORT-2), total Hg = oyster tissue (NIST SRM-1566b), and  $MeHg^+$  = fish protein (NCR DORM-4).

coefficients of between 3.7% and 9.5%, which satisfied the AOAC (2013) recommendations under the conditions studied. The linearity of the analytical curves was determined from the correlation coefficient, obtaining values with  $r^2 \ge 0.999$ . Three fortification levels were used in the determination of Sn at 100, 500, and 5000 µg kg<sup>-1</sup>, since this element does not present a certified value in the reference materials used. The recovery values varied from 89 ± 0.8% to 92 ± 1.2%, and values obtained for LOD and LOQ were 94 and 314 µg kg<sup>-1</sup>, respectively.

# **Results and discussion**

# Inorganic contaminants in canned tuna

Table 2 shows the results obtained for the contents of Cd, Pb, Sn, Hg, and  $MeHg^+$  in the different samples of canned tuna.

The samples of canned tuna conserved in oil showed the highest mean contents of Cd (85  $\mu$ g kg<sup>-1</sup>) and Pb (44  $\mu$ g kg<sup>-1</sup>), those in water showing smaller mean contents of Cd (20  $\mu$ g kg<sup>-1</sup>) and Pb (<30  $\mu$ g kg<sup>-1</sup>). Sn was not found in any of the samples (<94  $\mu$ g kg<sup>-1</sup>), inferring that the lacquer used as the internal coating of the cans destined for the tuna samples was adequate.

The samples conserved in oil showed values for the inorganic contaminants varying from 12.8 to 213  $\mu$ g kg<sup>-1</sup> (Cd); not detected to 59.2  $\mu$ g kg<sup>-1</sup> (Pb); not detected (Sn); 44 to 402  $\mu$ g kg<sup>-1</sup> (total Hg), and 35 to 393  $\mu$ g kg<sup>-1</sup> (organic Hg). With respect to the canned tuna samples conserved in water, the following concentration intervals were found: not detected to 30.5  $\mu$ g kg<sup>-1</sup> (Cd); not detected to 33.6  $\mu$ g kg<sup>-1</sup> (Pb); not detected (Sn); 51–460  $\mu$ g kg<sup>-1</sup> (total Hg); and 41–460  $\mu$ g kg<sup>-1</sup> (organic Hg).

The results obtained for the inorganic contaminants present in the samples of canned tuna commercialised in Brazil were in agreement with those existent in the literature. Emami Khansari et al. (2005) found values of between 50 and 72  $\mu$ g kg<sup>-1</sup> for Cd in canned tuna commercialised in Iran, whereas a mean value of 80  $\mu$ g kg<sup>-1</sup> of Cd was determined by Duran et al. (2014) for canned tuna from Turkey. Studies carried out with samples of canned tuna from Libya (Voegborlo et al. 1999), Saudi Arabia (Ashraf et al. 2006), and Iran (Ganjavi et al. 2010) showed elevated mean values of 180, 160, and 150  $\mu$ g kg<sup>-1</sup> of Cd, respectively. In the present study, the values found for the Cd content were between not detected and 213  $\mu$ g kg<sup>-1</sup>.

The evaluation of the canned tuna samples conserved in oil showed that 20% of these samples surpassed the MLs for Cd established by Brasil (ANVISA -RDC-42, 2013) and by Commission Regulation (EC) 1881/2006 (EC 2006) of 0.1 mg kg<sup>-1</sup> (100  $\mu$ g kg<sup>-1</sup>). This element is known to accumulate in the human organism, causing renal dysfunction and compromising the reproductive system (European Commision 2006).

With respect to Pb, low concentrations were found in this study (not detected to 59.2  $\mu$ g kg<sup>-1</sup>), the values being compatible with those reported for canned tuna commercialised in the regions of Alabama and Georgia in the USA (Ikem & Egiebor 2005), with mean values of 31  $\mu$ g kg<sup>-1</sup>. The concentrations found in the present study were lower than the interval of 90–400  $\mu$ g kg<sup>-1</sup> obtained by Uluozlu et al. (2007) for samples commercialised in Turkey. None of the samples analysed in the present study surpassed the limit value of 0.3 mg kg<sup>-1</sup> (300  $\mu$ g kg<sup>-1</sup>) established by CAC (2015), further defined by Commission Regulation (EC) 1881/2006 (EC 2006) and for Brazilian legislation Brasil (ANVISA - RDC-42, 2013).

Total mercury and methylmercury (MeHg<sup>+</sup>) were detected in all the samples, with values from 44 to 402  $\mu$ g kg<sup>-1</sup> of total Hg and from 35 to 393  $\mu$ g kg<sup>-1</sup> of MeHg<sup>+</sup> in the samples conserved in oil; and from 51 to 460  $\mu$ g kg<sup>-1</sup> of total Hg and from 41 to 460  $\mu$ g kg<sup>-1</sup>

Table 2. Mean values and concentration range ( $\mu$ g kg<sup>-1</sup>) for Cd, Pb, Sn, and Hg obtained for canned tuna conserves. Each brand was evaluated in three batches.

	Water conserve Mean (range)				Oil conserve Mean (range)					
	Brand 1	Brand 2	Brand 3	Brand 4	Brand 5	Brand 1	Brand 2	Brand 3	Brand 4	Brand 5
Cd	26	18	21	12	18	32	85	19	13	15
	(13–35) <sup>a</sup>	(nd –37) <sup>*ab</sup>	(14–29) <sup>*ab</sup>	(nd–16) <sup>b</sup>	(17–21) <sup>*ab</sup>	(18–51) <sup>*ab</sup>	(15–213) <sup>a</sup>	(17–22) <sup>b</sup>	(12–14) <sup>b</sup>	(12–18) <sup>b</sup>
Pb	46	34	38	45	40	31	37	33	44	33
	(nd–64) <sup>a</sup>	(nd–45) <sup>b</sup>	(nd–51) <sup>*ab</sup>	(38–53) <sup>a</sup>	(32–47) <sup>*ab</sup>	(nd–33) <sup>b</sup>	(nd–49) <sup>*ab</sup>	(nd–47) <sup>b</sup>	(30 – 63) <sup>a</sup>	(nd–42) <sup>b</sup>
Sn	nd**	nd**	nd**	nd**	nd**	nd**	nd**	nd**	nd**	nd**
Total Hg	143	185	261	183	83	129	174	232	236	68
-	(120–162) <sup>b</sup>	(116–251) <sup>*ab</sup>	(98–460) <sup>a</sup>	(165–214) <sup>*ab</sup>	(51–137) <sup>b</sup>	(116–148) <sup>*bc</sup>	(104–248) <sup>*ab</sup>	(185 – 273) <sup>a</sup>	(132–402) <sup>a</sup>	(44–103) <sup>c</sup>
MeHg <sup>+</sup>	142	187	258	177	69	115	167	195	240	47
-	(120–159) <sup>*bc</sup>	(106–273) <sup>*ab</sup>	(88–460) <sup>a</sup>	(152–212) <sup>*abc</sup>	(41–121) <sup>c</sup>	(97–140) <sup>*ab</sup>	(103–158) <sup>a</sup>	(163–213) <sup>a</sup>	(145–393) <sup>a</sup>	(35–89) <sup>b</sup>

\*Values followed by different letters on the same line differ significantly by the Tukey's test ( $p \le 0.05$ ).

\*\*nd = not detected. <8.5  $\mu$ g kg<sup>-1</sup> for Cd, <30  $\mu$ g kg<sup>-1</sup> for Pb; <94  $\mu$ g kg<sup>-1</sup> for Sn (LOD method detection limit).

of MeHq<sup>+</sup> for those conserved in water. In canned tuna samples from New Jersey (USA), Burger and Gochfeld (2004) found mean contents of 431 and 419  $\mu$ g kg<sup>-1</sup> for total Hg in samples conserved in water and oil, respectively. Martorell et al. (2011) found a mean value of 222  $\mu$ g kg<sup>-1</sup> of total Hg in canned tuna commercialised in Catalunha (Spain). In the study developed by Dabeka et al. (2014) in canned tuna samples from Canada, the highest average concentration obtained for total Hg was 325  $\mu$ g kg<sup>-1</sup> in Albacore tuna, whilst the lowest levels for Yellowfin tuna averaging 66 µg kg<sup>-1</sup>. Also Kral et al. (Forthcoming) examined canned fish samples acquired at local markets in the Czech Republic in terms of species and different FAO fishing area with. The analysis performed for different fish species demonstrated the highest total Hg content in tuna with average value of 170  $\mu$ g kg<sup>-1</sup>. These studies only evaluated the levels of total Hg, but it is important to determine MeHg<sup>+</sup> as well since this is considered to be the most toxic form of the Hg species.

Figure 1 shows the ratio in per cent between the organic (MeHg<sup>+</sup>) and total forms of Hg present in the different samples of canned tuna studied. The ratio of organic Hg (MeHg<sup>+</sup>)/total Hg varied from 82% to 99% for all the samples of canned tuna. The results showed the predominance of the most toxic form of Hg, that is the organic form, and according to Horvat and Gibicar (2005), in general the species MeHg<sup>+</sup> predominates in fish. In a study carried out by Paiva et al. (2016) with samples of tuna sushi commercialised in the southeast of Brazil, higher total Hg contents were obtained (45–761  $\mu$ g kg<sup>-1</sup>) for the tuna with ratios of organic Hg/total Hg varying from 69% to 99%.

Based on the earlier findings, it can be seen there is a greater propensity for total mercury to concentrate in fresh tuna, with lower concentrations in the canned tuna, but there is a predominance of the toxic organic species of mercury (MeHg<sup>+</sup>) in the latter. In the work developed by García et al. (Forthcoming) in canned tuna commercialised in Galícia, Spain, higher levels of total mercury were also observed in the fresh tuna in



Figure 1. Ratio between MeHg<sup>+</sup>/Total Hg in canned tuna oil and water conserves.

relation to that found in the technologically processed tuna, with mean values of 765 and 305  $\mu$ g kg<sup>-1</sup>, respectively. This tendency was confirmed by data found in the literature, reporting that larger, older fish could accumulate larger concentrations of mercury (Storelli et al. 2010; Yang et al. 2015). As reported by Knowles et al. (2003) and Ruelas-Inzunza et al. (2011), the larger fish are usually destined to be consumed fresh.

In the work developed by Burger and Gochfeld (2004), no difference was found between the total mercury concentrations in fish conserved in water and fish conserved in oil. However, Yess (1993) reported a mean value of 60  $\mu$ g kg<sup>-1</sup> of total mercury in 26 samples of tuna conserved in oil as against 110  $\mu$ g kg<sup>-1</sup> in 106 samples conserved in water.

# Estimate of the ingestion of Cd, Pb, and Hg due to the consumption of canned tuna and evaluation of the risk of exposure

The estimate of the exposure to the inorganic contaminants Cd, Pb, and total Hg and to methylmercury due to the consumption of canned tuna was calculated considering a 135 g portion, defined as drained weight samples.

**Cadmium (Cd**): CODEX (CAC 2015) has established a value of 25  $\mu$ g kg<sup>-1</sup> of body weight as the PTMI (provisional tolerable monthly intake) for Cd. Considering the highest value encountered of 213  $\mu$ g kg<sup>-1</sup>, an average 60 kg adult would have to consume 52 cans (7 kg) in order to characterise a risk. Hence the low values found for cadmium in the tuna samples indicate that the exposition to Cd from the consumption of canned tuna is not significant. Cadmium is an element that can be present in the air, soil, and waterbodies, due to anthropogenic and industrial activities in general (Barone et al. 2015).

Lead (Pb): In 2010, CODEX removed the provisional tolerable weekly intake (PTWI) for lead due to studies that showed that the previously established value of 25  $\mu$ g kg<sup>-1</sup> of body weight caused a loss of 3 points on a child's IQ and an increase in blood pressure in adults, when exposed to lead (CAC 2015). Thus, MLs were established for Pb in the different classes of food, the ML for fish being 0.3 mg kg<sup>-1</sup> (300  $\mu$ g kg<sup>-1</sup>), in agreement with Brazilian legislation (RDC 42, 2013) and with Commission Regulation (EC) 1881/2006 (EC 2006). In this study, the highest mean value found for Pb was 44  $\mu$ g kg<sup>-1</sup>, with minimum and maximum values of 33.4 and 59.2  $\mu$ g kg<sup>-1</sup>, respectively. These concentrations are below the maximum established limits, indicating that exposure to this contaminant by consuming canned tuna was not significant.

Lead and its components can enter the environment during mining, smelting, treatment, use, recycling, or elimination, and can be rejected in aquatic environments, thus contaminating fish and marine organisms (Okyere et al. 2015).

Total and organic mercury (total Hg; MeHg<sup>+</sup>): The CODEX Committee for Food Contaminants (CAC 2015) established a PTWI of 4  $\mu$ g kg<sup>-1</sup> of body weight for total Hg, and 1.6  $\mu$ g kg<sup>-1</sup> of body weight for MeHg<sup>+</sup>. In the present study, mean concentrations of 169 and 154  $\mu$ g kg<sup>-1</sup> of total Hg and MeHg<sup>+</sup>, respectively, were found in the canned tuna samples conserved in oil. Considering an adult weighing 60 kg and a 135 g portion of canned tuna (1 can), he would have to consume 11 cans (approximately 1.5 kg) or 5 cans (675 g) of tuna per week to reach the established ingestion limit for total Hg and MeHg<sup>+</sup>, respectively. Similarly, for the samples conserved in water, mean contents of 173 and 160  $\mu$ g kg<sup>-1</sup> were found for total and organic Hg, respectively, thus requiring the ingestion of 10 cans (1.4 kg) or 4 cans (540 g) per week to reach 100% of the PTWI for total and organic Hq, respectively.

The ingestion of fish containing MeHg<sup>+</sup> is recognised as being the principal route for human exposure to Hg and, due to its capacity for bioaccumulation throughout the trophic chain, this chemical species can reach high concentrations, principally in predatory fish (Horvat & Gibicar 2005). With respect to toxicology, organic Hg species are known to cross placental barriers and induce alterations in normal brain development in fetuses and newborn babies, and even cause neurological alterations in adults when present in elevated concentrations (FAO/WHO 2011).

# Conclusions

- With respect to cadmium, 20% of the tuna samples conserved in oil surpassed the ML of 100  $\mu$ g kg<sup>-1</sup> permitted by the Brazilian and European Commission legislation.
- Organic Hg/total Hg ratios above 82% were observed in the canned tuna samples.
- The consumption of just four cans (540 g) of tuna conserved in water or five cans (675 g) conserved in oil was sufficient to surpass the PTWI for MeHg<sup>+</sup> by 100% (PTWI for MeHg<sup>+</sup> = 1.6  $\mu$ g kg<sup>-1</sup>). Thus, it is important to include different varieties of fish in the diet, especially consumers in the groups of risk, such as pregnant and lactating women and children, in order to avoid a restricted consumption of tuna.

- The results obtained for Pb for the tuna samples presented values below the MLs of the Brazilian legislation.
- All the tuna samples analysed presented Sn contents below the detection limits of the method used.

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