Evaluation of toxic metals in canned fish market in Tehran

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Abstract

Introduction: Fish meat may be contaminated to toxic metals during commercial transport and processing depending on the raw material before processing occurs. Therefore, monitoring of these products is important with respect to toxic elements affecting human health.

Objective: The aim of this study is to assess toxic metals in canned fish marketed in Tehran,Iran.

Methods: This study based-cross-sectional was carried out in five different Iranian brands. Forty six canned fishes from this brands elected and toxic metal were determined using the flame and graphite furnace atomic absorption spectrometry after microwave digestion. The accuracy of the method was ascertained by standard reference material (NRCC-DORM-2 Dogfish Muscle).

Result: In this study was observed that some cases may be containing iron, lead and mercury above the legal limit set by the health authorities. The concentration of the toxic metals in the canned fish samples were found to be in the ranges of 1.29 - 2.45 µg/g, , 8.34 - 36.4 µg/g, 1.20 - 2.70 µg/g, 11.2 - 28.3 µg/g, 1.30 - 3.65 µg/g, 0.49 - 2.15 µg/g, 0.90 - 1.87 µg/g, 0.58 - 1.04 µg/g, 0.18 - 0.38 µg/g, and 0.03 - 0.12 µg/g for copper, zinc, manganese, iron, selenium, aluminum, chromium, nickel, lead and cadmium, respectively.

Conclusion: Comparison of the results obtained in this study with the values reported in literature showed that the consumption of the five (5) brands of the canned tuna does not pose any risk to the health of consumers particularly with respect to zinc, copper, cadmium and tin concentrations; though some of the brands contained iron, lead and mercury above the legal limits set up by some health authorities. It was, however, recommended that comprehensive and periodic monitoring of the trace metals in the canned tuna must continue to ensure the protection of the health of the consumers.

Keywords: Trace metals; canned fish; Atomic absorption spectrometry; Food safety; Contamination.

1. Introduction

In the past decade, popular demands for healthy food supply (lack of food contaminated with pesticides, heavy metals, etc.) has increased(1). Toxic metals are among the major contaminants of vegetables and fruits (2). Toxic metals are not biodegradable, have long biological half-life and have the potential to accumulate in various organs of the body can lead to unwanted side effects.(3). Most toxic metals are extremely toxic, and because of their solubility in water, contamination may readily reach toxic levels(4). Contamination of the food chain is one of the important ways for the entry of these toxic pollutants into the human body (5). The most important forms of aquatic pollution are heavy metals since they accumulate in aquatic organisms and may be transferred to humans through the food chain (6). Fish are very important human foods, but they are exposed to chemicals in polluted and contaminated waters (7). Therefore, they may accumulate potentially toxic minerals and represent one of the major sources of heavy metals for humans. Predator fish, in particular, may accumulate these substances more than the others (8)Tuna, as a predator, is able to concentrate large amounts of heavy metals, and this species is commonly consumed as canned (9). It is known that fish may also be contaminated by heavy metals during commercial processing like canning. So, information on the metal content in canned fish is important to ensure that it is safe for human consumption (7).Therefore most countries monitor the levels of heavy metals that may occur due to the commercial handling and processing(10).

Canned tuna fish are largely eaten in many countries, such as Libya, USA, Portugal, the Kingdom of Saudi Arabia, and Iran (8, 11, 12). Research carried out with respect to the trace metal content of canned tuna from Iran, suggest that very little comparative data are available.

Therefore, this study aimed to determine the levels of trace heavy metals (copper, zinc, manganese, iron, selenium, aluminum, chromium, nickel, lead and cadmium) in canned fish samples produced and marketed in Iran were done by flame and graphite furnace atomic absorption spectrometry after microwave digestion.

2. Materials and methods

2.1. Sampling

During the year 2012, five different Iranian brands (A, B, C, D, and E) of canned tuna (180g each) were analyzed to determine the level of trace metals (copper, zinc, manganese, iron, selenium, aluminum, chromium, nickel, lead, cadmium and mercury).

2.2. Reagents

All reagents were of analytical grades unless otherwise stated. Double deionized water (Milli-Q Millipore 18.2 MX cm^{-1} resistivity) was used for all dilutions. HNO_3, H_2O_2, and HCl were of suprapur quality (E. Merck). All the plastic and glassware were cleaned by soaking in dilute HNO_3 (1 + 9) and were rinsed with distilled water prior to use. The elements' standard solutions used for calibration were produced by diluting a stock solution of 1000 mg/l of the given element supplied by Sigma and Aldrich.

2.3. Apparatus

A Perkin Elmer A Analyst 700 atomic absorption spectrometer with deuterium background corrector was used in this study. The operating parameters for working elements were set as recommended by the manufacturer. Selenium, aluminum, chromium, nickel, lead and cadmium in canned fish samples were determined by HGA graphite furnace, using argon as inert gas. The other elements were determined in an air-acetylene flame. A Milestone Ethos D microwave closed system (maximum pressure 1450 psi, maximum temperature 300 _C) was used during the digestion process to extract the metals.

2.4. Microwave digestion

One gram of the sample was digested with 6 ml of concentrated HNO_3 (Suprapure, Merck) and 2 ml of concentrated H_2O_2 (Suprapure, Merck) in a microwave digestion system and diluted to 10 ml with the deionized water (Milli-Q Millipore 18.2 MX cm^{-1} resistivity). A blank digest was carried out in the same way (digestion conditions for microwave system applied were: 2 min for 250 W, 2 min for 0 W, 6 min for 250 W, 5 min for 400 W, 8 min for 550 W, vent: 8 min, respectively). In order to validate the method for accuracy and precision, certified reference materials (NRCC-DORM-2 Dogfish Muscle) were analyzed for corresponding elements.

3. Results and discussion

The recovery values obtained were higher than 95% for the microwave digestion method. The relative standard deviations were less than 10% for all the investigated elements. The student t test was used in this study ($p < 0.05$). The accuracy of the method was evaluated by means of trace metals determination in standard reference material (SRM). The results obtained were in good agreement with the certified values. The results for this study are given in Table 1. Detection limit is defined as the concentration corresponding to three times the standard deviation of 10 blanks. Detection limit values of the elements, as milligrams per liter in flame AAS were found to be 0.007 for copper, 0.014 for zinc, 0.008 for iron, 0.009 for manganese. Selenium, aluminum, chromium, nickel, lead and cadmium were below detection limits of the flame AAS. These elements were determined by graphite furnace AAS, using different matrix modifiers.

According to the results (Table 2), the metal contents in the samples studied depend on the analyzed species. All metal concentrations were determined on a wet weight basis. The contents of investigated trace metals in canned fish samples were found to be in the range of 1.10–2.50µg/g, 1.29–2.45µg/g, 8.34–36.40µg/g, 1.20–2.70µg/g, 11.20–28.30µg/g, 0.87–3.65µg/g, 0.49–1.65µg/g, 0.90–1.60µg/g, 0.18–0.38µg/g, and 0.05–0.25µg/g, for copper, zinc, manganese, iron, selenium, aluminum, chromium, nickel, lead and cadmium, respectively. Zinc was observed to be in the highest concentration, followed by iron and manganese.

In this study the lowest and highest copper levels were found in brand E and brand B, as 1.29 µg/g and 2.49µg/g, respectively, and there was no significant difference ($p > 0.05$) between the brands. Copper levels in canned fish samples have been reported in the ranges of 0.01–5.33 µg/g and 0.08-0.28 µg/g (7). The minimum and maximum copper levels in Turkish canned fish samples have been found to be in the range of 7.1–45.7 µg/g(13). Copper is essential for good health, but over dose intake it can cause adverse health problems, including liver and kidney damage(14). Copper concentrations in the analyzed canned fish samples were below the MAFF guideline value of 30 mg Cu/kg (15).

Zinc deficiency in human can be lead to loss of appetite, growth disorders, skin diseases and immune disorders. The maximum zinc level permitted in fish is 50 mg/kg (16). The recommended daily intakes of zinc and copper are 15mg and 12mg Zn for adult males and females, respectively; and 1.5–3.0mg Cu for both genders (17). The highest and lowest zinc contents were found to be 36.4µg/g in brand A and 8.34 µg/g in brand D. Zinc levels in canned fish samples have also been reported in the ranges of 0.14-97.8 µg/g,13.2-34.4µg/g, 8.20-12.4 µg/g (16, 18, 19). The lowest and highest zinc levels in Turkish canned fish samples have been found to be in the range of 33.8–566 µg/g (13, 20) reported the mean Zn value as 17.8mg/kg in canned tuna, commercialized in Turkey. However, Celik and Oehlenschlager (2007) analyzed three samples of canned tuna from two different Turkish brands and reported higher amounts of Zn than the permissible limits(13). It might be concluded that the amounts of trace metals in canned fish must be controlled comprehensively and periodically to ensure the protection of consumers' health.

The minimum and maximum manganese levels were found to be 1.20 µg/g in brand B and 2.70 µg/g in brand A samples. Manganese levels may be changed by food processing. Manganese contents in the literature have been reported in the range of 0.01–2.55 µg/g in canned fish samples (21), 1.56–3.76µg/g dry weight in fish samples of the middle Black Sea, Turkey (22) and 0.05–4.64 µg/g dry weight in fish species from Iskenderun Bay, Northeastern Mediterranean Sea, Turkey(23). Iron deficiency causes anemia and fish is one of the main sources of the metal. However, it is also known that, when their intake is excessively elevated the essential metals can produce toxic effects(8). Takatoku et al. (2007) observed that mammals are not able to excrete excess iron, and chronic iron overload was associated with slow and progressive failure of various organs(24). Iron contents in the literature have been reported in the range of 0.01–88.4µg/g in canned fish samples (7), 0.82–27.35 µg/g dry weight in fish species from North eastern Mediterranean Sea, Turkey (25), and 9.52–32.40 µg/g dry weight in fish samples of the middle Black Sea, Turkey (22). The lowest and highest iron contents were found to be 11.2 µg/g in brand C and 28.3 µg/g brand A samples.

Selenium is an essential trace element in animals and humans. It is important biological role as an antioxidant and as a regulator of thyroid hormone metabolism or as an anti-cancer agent. Low concentrations of selenium can cause abnormalities in living organisms and high concentrations are toxic. Canned fish samples in investigated in this study are very rich in selenium. The minimum and maximum selenium levels were found to be 1.30 µg/g in brand A and 3.65 µg/g in brand D. Selenium levels in canned fish samples have been reported to be in the range of 0.96-3.64 µg/g (18). There is limited information on selenium levels in fresh and canned fish.

Aluminum is not an essential element in human nutrition. Exposure to aluminum has been involved in a number of human diseases including encephalopathy / dialysis dementia, Parkinson's disease and Alzheimer's disease (26). The permissible aluminum dose for an adult is quite high, 60 mg per day (27)It is reported that maximum aluminum levels in some food samples are 15 mg/kg (28). Aluminum contents in the literature have been reported in the range of 0.02–5.41µg/g dry weight in fish species from Iskenderun Bay, North eastern Mediterranean Sea, Turkey (23), 0.032–5.346 µg/g wet weight in fish fillets baked and grilled in aluminum foil (29). The lowest and highest aluminum contents were found to be 0.49µg/g in brand B and 2.15µg/g in brand D.

The minimum and maximum Chromium levels were 0.90µg/g in brand D and 1.87µg/g in brand A samples. Chromium contents in the literature have been reported to be in the range of 0.0–0.30 µg/g in canned fish samples (19, 21, 30), and 0.07–6.46 µg/g dry weight in fish species from Iskenderun Bay, North eastern Mediterranean Sea, Turkey (31)and 0.97-1.70 µg/g wet weight in canned fish samples from Turkey (18). Chromium (III) is an essential nutrient that potentiates insulin action and thus influences carbohydrate, lipid and protein metabolism. Moreover, Cr (VI) has be reported to be carcinogenic(18)

The minimum and maximum nickel levels recorded in this study were 0.58µg/g in brand D and 1.04µg/g in brand A, respectively. Nickel contents in the literature have been reported to be in the range of 0.0-0.78 µg/g in canned fish samples(30) and 0.11-12.9 µg/g dry weight in fish species from Iskenderun Bay, Northeastern Mediterranean Sea, Turkey(23) and 0.50-0.85 µg/g wet weight in canned fish samples from Turkey(18). It is reported that maximum nickel level in some food samples is 0.2 mg/kg (16, 32).

Solder one of the sources of lead contamination in the canning process. Moreover, it is known that various types of fish were found to be contaminated with these metals. For this reason, monitoring the concentration of lead in canned fish is important for human health.(33). The lowest and highest lead levels were found to be 0.18µg/g in brand D 0.38µg/g in brand A samples, and there were no significant differences ($p > 0.05$) between the Pb content of samples obtained from the different brands. Lead contents have been reported in the literature to be in the range of 0.0-0.03 µg/g in canned fish samples (30), 0.09-6.95µg/g dry weight in fish species from Iskenderun Bay, North eastern Mediterranean Sea, Turkey (34), 0.22- 0.85 µg/g dry weight in fish samples of the middle Black Sea (22), 0.18-0.40 µg/g in canned tuna fish(33), 0.076–0.314 µg/g in Turkish canned fish samples (13), 0.0162-0.0726 µg/g in canned tuna fish ((33), 0.09-0.40 µg/g wet weight in canned fish samples from Turkey(18) and 0.09-0.45 µg/g in different brands of Turkish canned tuna (8). The maximum lead level permitted for canned fishes is 0.2 mg/kg according to the European communities (Commission of the European Communities, 2001). The fact that toxic metals are present in high concentrations in fishes is of particular importance in relation to the FAO/WHO (1976) standards for Pb and Cd as toxic metals. The maximum permissible doses for an adult are 3 mg Pb and 0.5 mg Cd per week, but the recommended doses, only one-fifth of this amount(35).

Lead reduced cognitive development and intellectual performance in children and increased blood pressure and cardiovascular disease in adults. (Commission of the European Communities, 2002)(36).

Cadmium accumulates in the body and may cause kidney dysfunction, skeletal damage and cause infertility. Cadmium concentrations in analyzed canned fish samples were higher than the European communities, with the maximum being 0.05 mg Cd/kg (Commission of the European Communities, 2002)(37). The lowest and highest cadmium levels were 0.05µg/g in brand C and 0.35 µg/g in brand D. Cadmium contents in the literature have been reported in the range 0.0-0.05 µg/g in canned fish samples(30), 0.01-4.16 µg/g dry weight in fish species from North eastern Mediterranean Sea, Turkey and 0.09-0.48 µg/g dry weight in fish samples of the middle Black Sea (22), 0.09- 0.32 µg/g in canned tuna fish (38), 0.025-0.494 µg/g in Turkish canned fish samples (13), and 0.0046–0.0720 µg/g in canned tuna fish and (33), 0.06-0.25 µg/g wet weight in canned fish samples from Turkey(18) and 0.01-0.02 µg/g in different brands of Turkish canned tuna (39).

Mercury can cause neurological disorders and some diseases. The maximum amount of mercury in tuna is observed. FDA has been set the maximum limit of 1.0 mg / kg for tuna. (30). Lourenc *et al*. (2004) were studied the toxic metal levels of canned seafood and reported the highest Hg value for canned tuna, but they mentioned that these values were still below the limits (1.0 mg/kg)(40). The average Hg contents was 0.01 mg/kg in Iranian canned tuna, it was 0.29 mg/kg in Libyan canned tuna (33). In literature, have been reported in the range 0.06-0.30 µg/g in different brands of Turkish canned tuna (35). In this study, the average Hg values were also below this limit and determined as 0.03 mg/kg for the samples of brand A, 0.04 mg/kg for brand B, 0.12 mg/kg for brand C, 0.06 mg/kg for brand D and 0.08 for brand E ($p > 0.05$).

Conclusions

In this study, the levels of copper, zinc, manganese, iron, selenium, aluminum, chromium, nickel, lead, cadmium and mercury in samples of canned fish marketed in Tehran is reported. Canned re Therefore, monitoring of these products is important with respect to toxic elements affecting human health. These results showed that there is no risk in canned tuna with respect to the concentrations of zinc, copper, cadmium and tin. However, it was observed that some of the samples may contain iron, lead and mercury above the legal permissible limits set by health authorities. These results may provide useful information for the assessing of toxic metal intake from this source.

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Table 1 Trace metal concentrations in certified reference material (NRCCDORM- 2 Dogfish Muscle), N = 15, and experimental recoveries

Element	*Certified value (μg/g)*	*Experimental value (μg/g)*	*Recovery (%)*
Cu	***2.34***	***2.28 ± 0.25***	***97***
Zn	***25.6***	***25.8 ± 0.96***	***102***
Mn	***3.66***	***3.49 ± 0.20***	***95***
Fe	***142***	***140.1 ± 7.80***	***99***
Se	***1.4***	***1.36 ± 0.10***	***97***
Al	***10.9***	***10.6 ± 0.15***	***98***
Cr	***34.7***	***33.1 ± 3.80***	***95***
Ni	***19.4***	***18.8 ± 0.74***	***97***
Pb	***0.065***	***0.063 ± 0.003***	***96***
Cd	***0.043***	***0.042 ± 0.002***	***97***

Table 2 Concentrations (μg/g) of trace metals in different brands of Tehran canned tuna**.**

Sample	Cu	Zn	Mn	Fe	Se	Al	Cr	Ni	Pb	Cd	Hg
A(n=15)	1.67 ± 0.12	36.4 ± 1.5	2.70 ± 0.25	28.3 ± 1.4	1.30 ± 0.12	0.95 ± 0.08	1.87 ± 0.10	1.04 ± 0.10	0.38 ± 0.04	0.14 ± 0.01	0.03 ± 0.01
B(n=15)	2.45 ± 0.10	18.2 ± 0.9	1.20 ± 0.10	14.9 ± 1.2	2.62 ± 0.15	0.49 ± 0.14	1.18 ± 0.12	0.85 ± 0.16	0.20 ± 0.01	0.08 ± 0.01	0.04 ± 0.01
C(n=15)	1.34 ± 0.10	9.31 ± 0.60	1.52 ± 0.23	11.2 ± 0.8	1.87 ± 0.07	0.71 ± 0.05	1.16 ± 0.23	0.72 ± 0.03	0.25 ± 0.02	0.05 ± 0.02	0.12 ± 0.02
D(n=15)	1.88 ± 0.12	8.34 ± 0.45	2.31 ± 0.15	18.4 ± 1.3	2.71 ± 0.24	1.12 ± 0.10	0.90 ± 0.09	0.62 ± 0.15	0.18 ± 0.03	0.21 ± 0.01	0.06 ± 0.02
E(n=15)	1.29 ± 0.15	15.2 ± 1.2	1.24 ± 0.12	13.8 ± 1.5	3.65 ± 0.35	2.15 ± 0.12	1.54 ± 0.10	0.58 ± 0.20	0.24 ± 0.01	0.35 ± 0.02	0.08 ± 0.01