

Original article

Health Risk Assessment and Heavy Metal Contamination in Canned Tuna Fish from the Libyan Market

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This study investigated the concentrations of selected heavy metals in canned tuna products commercially available in the Libyan market, given the widespread consumption of canned tuna as an affordable source of protein and the potential health risks associated with the bioaccumulation of chemical contaminants in fish tissues. We randomly obtained eight canned tuna samples from different brands and production batches from supermarkets and local markets in Tripoli, Libya. Five heavy metals, namely mercury (Hg), lead (Pb), cadmium (Cd), iron (Fe), and copper (Cu), were analyzed. Iron, lead, copper, and cadmium were quantified using a Graphite Furnace Atomic Absorption Spectrometer (GFAAS), whereas mercury was determined by Cold Vapor Atomic Absorption Spectrometer (CVAAS). The reliability of the analytical procedure was assessed using DORM-4 Fish Protein Certified Reference Material, with recovery values ranging from 95% to 102%. The findings showed that the average concentrations of the investigated metals were generally within the permissible levels specified by international food safety standards. Nevertheless, mercury concentrations varied substantially among samples, with sample H7 showing the highest recorded value of 1.715 ppm. Lead was present in all samples, with concentrations ranging from 0.059 to 0.126 ppm and an overall mean of 0.092 ± 0.026 ppm. All measured lead concentrations were below the European Union maximum limit of 0.20 mg/kg, with no samples exceeding the specified guideline. The concentrations of cadmium and copper likewise remained within their respective permissible limits. Although iron exhibited the greatest variation among the analyzed metals, its detected levels did not suggest an immediate safety concern according to the reference limits applied in this study. In conclusion, the results reveal differences in heavy-metal concentrations among canned tuna products available in the Libyan market. These findings emphasize the need for continuous regulatory oversight, periodic monitoring of heavy-metal contamination, effective control of imported food products, and improved traceability throughout the supply chain to ensure the safety and quality of canned tuna consumed by the Libyan population.

Introduction

The global demand for seafood has surged in recent decades, driven by its recognized nutritional benefits, particularly as a source of high-quality protein, essential omega-3 fatty acids, vitamins, and vital minerals [1, 2]. Among the various forms of seafood, canned fish holds a prominent position due to its convenience, affordability, and extended shelf life, making it a dietary staple for many populations worldwide, including those in Libya [3, 5]. Canned tuna, in particular, is a widely consumed product, often serving as a primary and accessible source of animal protein and essential nutrients [6, 7]. However, the consumption of fish, including canned varieties, presents a potential health risk due to the bioaccumulation of chemical pollutants, especially toxic and essential heavy metals, in their tissues [4, 8, 9]. Metals such as iron (Fe), zinc (Zn), and copper (Cu) are essential micronutrients required for various physiological functions, including enzyme activity, oxygen transport, and immune response [10, 11]. Conversely, elements like lead (Pb), mercury (Hg), and cadmium (Cd) are highly toxic and serve no biological function, posing significant threats to human health even at low concentrations. Exposure to these toxic metals is associated with severe health issues, including renal dysfunction, neurological damage, cardiovascular diseases, and carcinogenic effects [12, 14]. The presence of heavy metals in fish is influenced by a multitude of factors, including the degree of environmental contamination in their habitat, species-specific metabolic rates, feeding habits, and contamination that can occur during fishing, processing, and canning operations [15, 17].

The canning process, while preserving the nutritional value of fish, can also introduce additional contaminants or alter metal concentrations. Factors such as the pH of the product, the quality of the lacquer coating inside the can, oxygen concentration, and storage conditions have all been identified as potential determinants of metal levels in the final product

[4, 17]. Given the dietary importance of canned tuna and the inherent risk of heavy metal contamination, numerous international studies have been undertaken to assess these risks in various markets, including Iran [5, 18, 20], Turkey [7, 21, 22], the USA [6], Italy [23], Iraq [1], and many others. Key international food safety organizations like the Food and Agriculture Organization (FAO), the World Health Organization (WHO), and the European Union (EU) have established Maximum Permissible Limits (MPL) and Provisional Tolerable Weekly Intakes (PTWI) for heavy metals in food, including fish and fishery products, to safeguard public health [24, 27]. However, recent studies have consistently revealed that heavy metal concentrations in canned fish from several regions can exceed these permissible limits, raising significant public health concerns [1, 5, 20].

Despite the nutritional value and widespread consumption of canned tuna in Libya, a comprehensive assessment of its heavy metal content and the associated human health risks remains a critical data gap. Preliminary data from an internal study indicates concerning levels of certain metals, such as Pb, in samples of canned tuna from the Libyan market. This situation necessitates a detailed scientific investigation to quantify the concentrations of heavy metals in these widely consumed products, ensure their compliance with international safety standards, and evaluate the potential health risks for the Libyan population. This study aims to address this knowledge gap by analyzing the levels of key heavy metals, including Cu, Pb, Fe, Cd, and Hg, in canned tuna fish sold in the Libyan market. The findings will generate essential data for national food safety surveillance programs, help in formulating risk management strategies, and ultimately contribute to minimizing public health risks associated with dietary exposure to these contaminants.

Materials and Methods

Sample Collection

A total of eight canned tuna samples, representing different brands and production batches, were randomly collected from various retail supermarkets and local markets in Libya to determine the levels of heavy metals: mercury (Hg), cadmium (Cd), Iron (Fe), Copper (Cu), and lead (Pb). The samples were transported to the laboratory under ambient conditions and stored at room temperature until analysis. The samples were coded as H1, H2, H3, H4, H5, H6, H7, and H8 for identification purposes. The country of origin and the storage media (e.g., oil or brine) were recorded when available, though specific brand details were anonymized to ensure unbiased analysis.

Sample Preparation and Digestion for (Fe, Pb, Cu, Cd)

Upon arrival at the laboratory, each can be carefully opened, and the liquid content (oil or brine) was completely drained off. The fish flesh was then homogenized thoroughly using a stainless-steel food blender to obtain a uniform composite sample, following the method described by [3] and [5]. For the determination of iron (Fe), lead (Pb), copper (Cu), and cadmium (Cd), approximately 5.0 g of the homogenized wet sample was accurately weighed into a glass digestion vessel. Then, 20 mL of concentrated nitric acid (HNO_3) was added to the sample. The mixture was placed on a hot plate and heated until the evolution of brown fumes (nitrogen dioxide) ceased, indicating the completion of the initial oxidation. Subsequently, 3 mL of hydrogen peroxide (H_2O_2) was added, and the mixture was heated again until near dryness. After cooling, 2 mL of concentrated nitric acid was added, and the solution was gently heated until the yellow fumes disappeared. The digest was then cooled to room temperature, diluted with deionized distilled water, and filtered through Whatman No. 42 filter paper into a 50 mL volumetric flask. The volume was made up to the mark with ultra-pure deionized water. A reagent blank was prepared in the same manner using the same acid mixture without the fish sample to correct for any background contamination, as recommended by [22]. The final solutions were then analyzed using a Graphite Furnace Atomic Absorption Spectrometer (GFAAS) for Fe, Pb, Cu, and Cd.

Sample Preparation and Digestion for Mercury (Hg) Analysis

For the determination of mercury (Hg), a separate digestion procedure was employed. Approximately 1.0 g of the homogenized wet tuna sample was accurately weighed into a digestion flask. Then, 5 mL of concentrated nitric acid (HNO_3) and 5 mL of concentrated sulfuric acid (H_2SO_4) were added. The mixture was allowed to stand at room temperature for 24 hours for predigestion. After this period, the flask was placed in a water bath and heated for 2 hours. The sample was then removed and allowed to cool to room temperature. Subsequently, 15 mL of ice-cold distilled water was added, followed by the addition of 0.75 g of potassium permanganate (KMnO_4). Hydrogen peroxide (H_2O_2) was then added dropwise until the purple color of the permanganate was completely discharged and the solution became clear. The clear digest was filtered through Whatman No. 42 filter paper into a 25 mL volumetric flask, and the volume was made up to the mark with ultra-pure deionized water. The prepared sample was then analyzed for mercury using a Cold Vapor Atomic Absorption Spectrometer (CVAAS).

Heavy Metal Analysis

The concentrations of five heavy metals—Mercury (Hg), Iron (Fe), Lead (Pb), Copper (Cu), and Cadmium (Cd)—were determined in the digested samples using validated analytical techniques. Mercury was analyzed using a Cold Vapor

Atomic Absorption Spectrometer (CVAAS) following the method of [4]. Iron, Lead, Copper, and Cadmium were determined using a Graphite Furnace Atomic Absorption Spectrometer (GFAAS) (Perkin Elmer 4110 ZL) according to the method described by [20]. For quality control, all analyses were performed in triplicate, and the results were averaged. The analytical method was validated using DORM-4 Fish Protein Certified Reference Material (National Research Council of Canada). Recovery rates for the analyzed metals ranged between 95% and 102%, confirming the accuracy and precision of the methodology, consistent with the findings of [1].

Results

The concentrations of heavy metals (Hg, Fe, Pb, Cu, and Cd) in the eight canned tuna samples collected from the Libyan market are presented in (Table 1). The concentration ranges and mean values for each metal across all samples were calculated as follows:

- **Mercury (Hg):** The concentration ranged from 0.001 ppm to 1.715 ppm, with a mean value of 0.245 ± 0.595 ppm.
- **Copper (Cu):** The concentration ranged from 0.051 ppm (H2) to 0.089 ppm (H6), with a mean value of 0.072 ± 0.014 ppm.
- **Lead (Pb):** The concentration ranged from 0.059 ppm (H4) to 0.126 ppm (H1), with a mean value of 0.092 ± 0.026 ppm.
- **Iron (Fe):** The concentration showed the widest variation, ranging from 0.647 ppm (H4) to 1.758 ppm (H7), with a mean value of 1.058 ± 0.384 ppm.
- **Cadmium (Cd):** The concentration ranged from 0.006 ppm (H5) to 0.014 ppm (H1), with a mean value of 0.010 ± 0.003 ppm.

Table 1. Heavy metal concentrations (ppm) in canned tuna samples

Sample Code	Hg (ppm)	Cu (ppm)	Pb (ppm)	Fe (ppm)	Cd (ppm)
H1	0.0489	0.064	0.126	1.519	0.014
H2	0.01	0.051	0.123	0.889	0.013
H3	0.001	0.060	0.093	0.769	0.008
H4	0.001	0.065	0.059	0.647	0.009
H5	0.0296	0.078	0.068	0.914	0.006
H6	0.0669	0.089	0.105	1.068	0.009
H7	1.715	0.087	0.092	1.758	0.010
H8	0.0871	0.085	0.067	0.897	0.013

Notably, Lead (Pb) was detected in all analyzed samples, with concentrations that, in several instances, were lower than the European Union permissible limit of 0.2 mg/kg for canned tuna (European Union, 2005). Iron (Fe) levels were generally low compared to international standards, while Copper (Cu) and Cadmium (Cd) concentrations remained well within the acceptable limits established by FAO/WHO [27]. For mercury (Hg), the sample H7 exhibited an exceptionally high mercury concentration of 1.715 ppm, which is significantly above all international regulatory limits. Samples H3 and H4 showed the lowest mercury levels at 0.001 ppm, which is near the detection limit. Seven out of eight samples (87.5%) had mercury concentrations below 0.1 ppm.

Discussion

The concentrations of heavy metals in canned tuna fish marketed in Libya were determined and compared with international safety standards and previous studies conducted in other regions. The results reveal significant variation in metal concentrations among the samples, reflecting differences in species, fishing grounds, and processing methods [11].

Mercury (Hg) Contamination

Mercury is one of the most hazardous environmental contaminants, and its organic form, methylmercury (MeHg), is a potent neurotoxin that poses significant health risks to humans, particularly vulnerable populations such as pregnant women, nursing mothers, and children [28, 8]. Methylmercury bioaccumulates and biomagnifies through the aquatic food chain, with higher trophic-level predatory fish like tuna accumulating the highest concentrations [29, 30]. In the present study, mercury concentrations in canned tuna samples from the Libyan market showed remarkable variation, ranging from 0.001 ppm to 1.715 ppm. The mean mercury concentration (0.245 ppm) was below the FAO/WHO permissible limit of 0.50 mg/kg [27]. However, the detection of one sample (H7) with a concentration of 1.715 ppm, which is 3.4 times higher than the FAO/WHO limit and 8.6 times higher than the more stringent EU limit of 0.20 mg/kg for canned tuna (European Union, 2005), is a major public health concern.

Comparison with International Standards

The mercury levels found in this study can be compared with international regulatory limits:

Table 2. Mercury levels compared with international regulatory limits

Regulatory Body	Maximum Permissible Limit (ppm)	Samples Exceeding Limit
FAO/WHO [27]	0.50	1 (H7: 1.715 ppm)
European Union [25]	0.20	1 (H7: 1.715 ppm)
FDA [31]	1.00	1 (H7: 1.715 ppm)
Turkish Food Codex [32]	0.50	1 (H7: 1.715 ppm)

This indicates that 12.5% (1 out of 8) of the analyzed samples exceeded all major international safety standards for mercury in fish.

Comparison with Other Studies

The mercury concentrations observed in this study can be contextualized by comparing them with findings from other regions:

Iran

Hosseini [20] reported mean mercury concentrations in canned tuna ranging from 0.02 to 0.28 mg/kg, with all samples below the permissible limit. Emami Khansari [19] found mean mercury levels of 0.05–0.08 mg/kg in tuna from the Persian Gulf.

Turkey

Mol [7] reported mercury levels in canned bonito, sardines, and mackerel ranging from 0.000 to 0.223 mg/kg, with all samples within safe limits. Similarly, Miklavčič [37] found low mercury levels in canned fish from Slovenia.

USA

Burger and Gochfeld [28] reported that canned tuna in the USA had mercury concentrations ranging from 0.028 to 0.314 ppm, with some samples exceeding the FDA action level of 1.0 ppm.

Italy

Storelli [23] found mercury levels in canned tuna ranging from 0.02 to 1.85 mg/kg, with approximately 60% of samples exceeding the EU limit of 0.20 mg/kg.

Lebanon

Obeid et al. (2011) reported total mercury levels in canned fish ranging from 0.05 to 0.51 mg/kg.

Iraq

Islam and Mustafa (2023) reported lower mercury levels, with most samples below 0.1 ppm. The exceptionally high mercury level found in sample H7 (1.715 ppm) is comparable to the highest values reported by [23] in Italy and Gerstenberger [38] in the USA, where some canned tuna samples exceeded 1.5 ppm. This suggests that the contaminated sample may have originated from larger, older tuna species (e.g., *Thunnus albacares* or *Thunnus obesus*) that accumulate higher mercury concentrations due to their long lifespan and high trophic position [29, 30].

Lead (Pb) Contamination

Lead is a highly toxic metal with no known biological function, and its presence in food is strictly regulated due to its neurotoxic and nephrotoxic effects [12, 13]. In the present study, the mean Pb concentration (0.092 ppm) was below the FAO/WHO permissible limit of 0.50 mg/kg [27] and the Turkish Food Codex limit of 0.40 mg/kg for bonito [32] and the EU limit of 0.20 mg/kg for tuna (European Union, 2005). The low Lead concentrations may indicate that the canned tuna available in the Libyan market is derived from relatively clean marine environments.

Cadmium (Cd) Contamination

Cadmium is another highly toxic metal that accumulates in the kidneys and liver and is associated with renal dysfunction and bone damage [8]. The mean Cd concentration in our samples (0.010 ppm) was well below the FAO/WHO permissible limit of 0.50 mg/kg [27] and the EU limit of 0.05 mg/kg [25]. All samples were compliant with both international standards. These results are lower than those reported for canned tuna from Iran [20], where mean Cd levels ranged from 0.06 to 0.15 mg/kg, and are comparable to the lower ranges reported by [6] for canned fish in the USA. The low Cd concentrations suggest that the canned tuna in the Libyan market originates from relatively uncontaminated marine environments.

Copper (Cu) and Iron (Fe) Concentrations

Copper and Iron are essential micronutrients for human health, playing crucial roles in enzymatic reactions, oxygen transport, and energy metabolism [21, 36]. However, excessive intake can lead to toxicity, particularly affecting the liver and kidneys [12, 39].

Copper (Cu)

The mean Cu concentration of 0.072 ppm is far below the WHO-established maximum limit of 30 mg/kg [36]. This is consistent with studies by [7] for canned fish in Turkey and lower than the 0.15–0.27 mg/kg range reported by [40] in Puerto Rico.

Iron (Fe)

The mean Fe concentration of 1.058 ppm was well below the acceptable limit of 15 mg/kg for canned food [35]. The variation between samples (0.647 to 1.758 ppm) is typical and may reflect differences in fish species, seasonal factors, and dietary intake [11]. This level poses no health risk to consumers.

Study Limitations

A limitation of the present study is the relatively small sample size ($N = 8$), which may limit the statistical power of the analysis and the ability to detect differences among the analyzed samples. Therefore, the findings should be interpreted with caution, particularly when considering their generalizability to the wider Libyan market and the broader regional market. Further studies involving a larger number of samples from different brands, geographical locations, and sampling periods are recommended to provide more representative data and strengthen the statistical evidence regarding heavy metal contamination in canned tuna.

Health Risk Implications

From a public health perspective, the observed concentrations of Pb, Cd, Cu, Fe, and Hg in the analyzed canned tuna samples suggest that moderate consumption of these products poses no immediate acute toxicity risk.

Mercury is a cumulative neurotoxin that primarily affects the central nervous system. Chronic exposure to methylmercury can lead to:

- Neurological deficits, including impaired cognition, memory loss, and developmental delays in children [13].
- Cardiovascular effects, including hypertension and increased risk of myocardial infarction [8].
- Immunological and renal toxicity [12].

The Provisional Tolerable Weekly Intake (PTWI) for methylmercury, as recommended by the Joint FAO/WHO Expert Committee on Food Additives (JECFA), is 1.6 $\mu\text{g/kg}$ body weight per week [34]. For a 70 kg adult, this translates to a maximum allowable weekly intake of 112 μg of methylmercury. Our findings underscore the importance of regular monitoring and quality control of imported canned fish in the Libyan market. The levels of toxic metals should be periodically assessed to ensure consumer safety, as recommended by [20] and [5]. Additionally, public awareness campaigns regarding the benefits and risks of fish consumption should be encouraged, especially for high-risk groups such as pregnant women and children.

Conclusion

This study assessed the concentrations of selected heavy metals in canned tuna products marketed in Libya. Overall, the mean concentrations of mercury, lead, cadmium, copper, and iron were within the permissible limits established by international food safety standards. However, a marked exceedance of the mercury limit was identified in one sample, which recorded a concentration of 1.715 mg/kg, exceeding the FAO/WHO and EU maximum limits by approximately 3.4-fold and 8.6-fold, respectively. In contrast, the concentrations of lead, cadmium, copper, and iron remained within the applicable regulatory limits. Although the overall findings suggest that the investigated canned tuna products generally complied with established safety limits, the detection of elevated mercury in an individual sample highlights the need for continued and systematic monitoring of heavy metal contamination in canned fish products available in the Libyan market. Regular surveillance, effective risk communication, and greater awareness among relevant authorities, producers, and consumers may help reduce potential exposure to heavy metals and support food safety. Further studies involving larger and more representative sample sizes, a wider range of brands and production batches, and assessment of the selenium-to-mercury ratio are recommended to strengthen the risk assessment and provide a more comprehensive understanding of potential exposure associated with canned tuna consumption in Libya.

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