

Determination of mercury concentrations in canned, fresh and frozen tuna in Tripoli markets in Libya and assessment of its risks to consumer health.

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Abstract

Fishes are considered as good indicators of heavy metals pollution in aquatic ecosystem in addition to being a good source of protein. Thus the level of Mercury (Hg) in fish which become a health hazard, was examined. The aim of the study was to determine the concentrations of Hg in the studied tuna fish samples. Moreover, evaluation of associated health risks from fish consumption were conducted of which, the intake rates of Hg was gauged based on Hg concentrations in fish muscles and the rate of daily fish consumption by Libyan population. A total of Forty-five specimens (20 canned tuna samples, local and imported samples, five frozen tuna samples and 20 fresh tuna samples) were sampled from different markets, large commercial centers, and food distribution points in the Tripoli area. A quantity of 0.5 grams of muscle completely homogenized mixture of each canned, fresh, and frozen tuna were digested by a mixture of 5 ml of nitric acid and 5 ml of sulfuric acid. A cold vapor atomic absorption spectrometer was utilized for the tuna fish analysis. The results showed that the concentrations of Hg were at the limits set by WHO and FAO, except for three frozen tuna samples were higher than the safety limits for human consumption, (2.33, 0.64, and 1.45 mg/kg wet. weight), and one fresh tuna sample (0.51 mg/kg wet. weight). The results revealed that, the average concentration of Hg for canned, frozen, and fresh tuna samples were calculated as 0.12, 1.02, and 0.19 mg/kg wet weight, respectively. However, the target hazard quotient (THQ) for Hg was less than 1 in the analyzed canned, frozen, and fresh tuna samples indicating no potential health risks to the population in studied area. However, the risk of health effects is increased due to the presence of Hg in seafood. Therefore, groups most at risk, including

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young children, the elderly, and pregnant women, limit their consumption of certain types of seafood, especially tuna. further comprehensive monitoring programs should be conducted.

Key words: mercury, risk assessment, canned tuna, Tripoli markets

الملخص

تُعتبر الأسماك مؤشرًا جيدًا لتلوث النظام البيئي المائي بالمعادن الثقيلة، بالإضافة إلى كونها مصدرًا جيدًا للبروتين. لذلك، تم تقدير مستوى الزئبق في الأسماك، والذي يُشكل خطرًا على صحة الناس والبيئة. هدفت الدراسة إلى تحديد تركيزات الزئبق في عينات أسماك التونة المدروسة. علاوة على ذلك، تم تقييم المخاطر الصحية المرتبطة باستهلاك الأسماك، حيث تم تحديد معدلات استهلاك الزئبق بناءً على تركيزات الزئبق في عضلات الأسماك ومعدل الاستهلاك اليومي للأسماك لدى السكان الليبيين. أُخذت خمس وأربعون عينة (عشرون عينة تونة معلبة، محلية ومستوردة، وخمس عينات تونة مجمدة، وعشرين عينة تونة طازجة) من أسواق مختلفة، ومراكز تجاربة كبري، ونقاط توزيع أغذية في منطقة طرابلس. تم هضم كمية 0.5 جرام من خليط متجانس تمامًا من كل من التونة المعلبة والطازجة والمجمدة، بمزيج من 5 مل من حمض النيتريك و5 مل من حمض الكبريتيك. أُجري تحليل الزئبق في العينات المدروسة باستخدام مطياف الامتصاص الذري بالبخار البارد. أظهرت النتائج أن تركيزات الزئبق كانت ضمن الحدود المسموح بها من قِبَل منظمتي الصحة العالمية والأغذية والزراعة، باستثناء ثلاث عينات التونة المجمدة تجاوزت حدود السلامة للاستهلاك البشري (2.33، 0.64، و1.45 ملغم/كغم وزن جاف)، وعينة تونة طازجة واحدة (0.51 ملغم/كغم وزن جاف). أظهرت النتائج أن متوسط تركيز الزئبق في عينات التونة المعلبة والمجمدة والطازجة 0.12 ملغم/كغم من الوزن الجاف، و1.02 ملغم/كغم من الوزن الجاف، و0.19 ملغم/كغم من الوزن الجاف، على التوالي. ومع ذلك، كان معدل الخطر المستهدف للزئبق أقل من 1 في عينات التونة المدروسة (المعلبة والمجمدة والطازجة)، مما يُشير إلى عدم وجود مخاطر صحية محتملة على السكان من استهلاك هذه الأسماك في المنطقة المدروسة. ومع ذلك، يزداد خطر الآثار الصحية بسبب وجود الزئبق في المأكولات البحرية. لذلك، يجب على الفئات الأكثر عُرضة للخطر، بما في ذلك الأطفال الصغار وكبار السن والنساء الحوامل، ان تقلل من استهلاك أنواع معينة من المأكولات البحرية، وخاصبة التونة. وينبغي إجراء المزيد من برامج الرصد والمراقبة الدورية الكاملة.

الكلمات المفتاحية: الزئبق، تقييم الضرر، التونة المعلبة، أسواق طرابلس

العدد الحادي عشر مارس March 2025 المجلد الثاني



1. Introduction

Water pollution is considered as the biggest problem, which threatens the aquatic organisms and has become critical environmental threat (Baldantioni *et al.*, 2004). Aquatic ecosystems exhibit significant sensitivity and vulnerability to numerous hazards, primarily due to the wide variety of pollutants generated by domestic, urban, and industrial activities, particularly in the aquatic environment (Sharma *et al.*, 2024; Olgunoglu *et al.*, 2025). When toxic metals are released into the environment, they contaminate the soil and accumulate in plants and organic tissues as they adversely affect the human health. The marine environment is also affected by natural phenomena that incorporate metals, trace elements and other compounds such as the upwelling of deep water containing nutrients and the dust or sand from deserts with metals (Raja *et al.*, 2009).

Due to the dynamism, complexity and the changing nature of marine ecosystems the contaminates that enter the waters, cause unwanted results, which in turn, directly or indirectly impact the environmental balance of the environment (Li *et al.*, 2017). The accumulation of heavy metals in marine ecology negatively impacts the ecosystems themselves and the fishes. The severity of heavy metals results in contamination of marine environment, which is very critical problem, especially human health. Emissions from industries and agricultural activities are considered as major source of pollution, especially in aquatic environment (Tarras-Wahlberg *et al.*, 2001).

Heavy metals are considered as a major aquatic frequently detected in coastal areas (Duffus, 2002; Li *et al.*, 2017). Contaminations of heavy metals are one of the extensive forms of marine pollution, as they do not rapidly decompose in marine environment, which deeply hinders the marine ecology due to the comparatively high concentrations and their toxicity even at low concentrations which affects the fishes and ultimately humans are affected through food web (Raja *et al.*, 2009). Bioaccumulation assessment is a critical indicator for monitoring the biogeochemical cycles of heavy metals within aquatic ecosystems (Al-Bakush and Abu-Qasim, 2019).

Mercury is one of natural heavy metals that could cause food-borne toxicities by contaminating different nutritional levels. This element is also an environmental pollutant due to the stability and the ability to accumulate in biologic tissues (Li *et al.*, 2017). Mercury is a highly toxic heavy metal; it accumulates and biomagnifies along the food chain, leading to higher concentrations in predatory fish (Garofalo *et al.*, 2025). The

العدد الحادي عشر مارس March 2025 المجلد الثاني



content of organic and inorganic mercury varies depending on the animal species, age, size, and water pH. However, methylmercury is the predominant form found in fish and other seafood (Alex, 2018; Garofalo *et al.*, 2025). Consuming foods containing high levels of Hg is particularly dangerous for pregnant women due to its teratogenic effects, and for children during neurodevelopment (Counter and Buchanan, 2004).

Living organisms accumulate metals in their tissues by bioaccumulation, which causes increase in the amount of these toxic in an organism's tissues as a result of the absorption rate exceeding the body's ability to eliminate these toxic substances. The degree of accumulation depends on factors such as the chemical nature of the contaminant, type of organism, its physiological state, water temperature and salinity (Embaby *et al.*, 2024). Fish living in aquatic systems contaminated with heavy metals are of great environmental concern, as these metals accumulate within various biological tissue structures (Hanis *et al.*, 2025; Al- Kazaghly *et al.*, 2025).

Fish, as a significant source of protein has been influenced by rapid industrialization and mechanized agricultural activities resulting to increase in the level concentration of heavy metals found in different varieties of fish (Embaby *et al.*, 2024). The species that accumulate heavy metals in their tissues are known as bio-monitors, these are used to measure the level of heavy metal pollution in the environment (Phillips and Rainbow 1993). Normally fishes are used as the standard for scrutinizing the environmental pollution in aquatic ecosystems. As the position of fish is the final level of the food chain, when consumed, the contaminated diversities will easily pass the metals into the humans (Burger and Gochfeld 2005).

Moreover, the fishes can better replicate the history of pollution of the sampling location due to their exposure to contaminants that amass over their life span. Fish also have been popular targets of heavy metal monitoring programs in marine environments because sampling, sample preparation and chemical analysis are usually simpler, more rapid and less expensive than alternative choices such as water and sediments (Rayment and Barry 2000). According to Erkan *et al.*, (2011), marine organisms especially fishes used to monitor heavy metals in the marine environment. However, it is essential to regularly monitor the chemical quality of aquatic organisms, especially the accumulations of toxic heavy metals, for maintaining the human health.

العدد الحادي عشر مارس March 2025 المجلد الثاني



Tuna fish, scientifically referred to as Thunnus and part of the scombridae family, is a pelagic and migratory marine species that gathers in large schools across the Atlantic, Pacific, and Indian Oceans (Norhazirah *et al.*, 2020). Tuna fish is the top predators in oceanic environments and play a vital role in marine ecosystems. They represent approximately 20% of the total economic value derived from marine fisheries, contributing significantly to meeting global protein demand (Voegborlo *et al.*, 1999; Dhaneesh *et al.*, 2014). The tuna fishery is the largest and most specialized of all commercial fisheries (Norhazirah *et al.*, 2020). The population typically relies on local and imported tuna in various forms, including fresh, canned, and frozen. This study aims to determine the Hg levels in canned tuna, frozen tuna and fresh tuna fish samples and assess their health risks to consumers in Libya.

2. Materials and Methods

2.1. Study area

This research was conducted from December 2023 to July 2024. Were the samples collected from Tripoli area Figure (1), which located in the northwestern sector of Libya. It is bordered to the north by the Mediterranean Sea, to the south by the administrative borders of Qasr Ben Ghashir, to the east by the district of Al-Qarabulli, and to the west by Alzawia city. The study area located between Longitude: 13° 11' 14.86" E Latitude: 32° 52' 30.68" N.



Fig. (1): the study area **2.2. Materials and reagents**

All materials used in this study except mercury standard solution (1000 ppm, Merck Company). Also, all laboratory glass wares were put in nitric oxide 10% for 24 h and rinsed with deionized distilled water prior the usage to prevent any mercury contamination.

العدد الحادي عشر مارس March 2025 المجلد الثاني



2.3. Sample collection:

A total of 45 comprehensive samples were collected from various markets, large shopping centers, and grocery stores in the Tripoli area. Twenty canned tuna samples were collected, including various types of canned tuna (local and imported). The content of one can is 80 g wet weight and is considered a single serving. five frozen tuna samples and 20 fresh tuna samples from aquaculture markets. After obtaining the frozen and fresh samples, they were transported in a manual container insulated with ice to ensure tissue integrity until they arrived at the marine chemistry and physics laboratory at the marine biology research center.

2.4. Samples preparation:

After arrival the samples to the laboratory, the samples were prepared for digestion by dissecting the tissue using plastic dissection tools. The muscle was isolated from the rest of the frozen and fresh tuna organs and mixed thoroughly to ensure complete homogeneity. The tuna fish muscles were separated from the brine (preservative) in the canned tuna sample and combined to form a homogeneous mixture. A precise quantity of 0.5 grams of the completely homogenized mixture of each canned, fresh, and frozen tuna (muscle) is measured and placed in a beaker. A mixture of 5 ml of nitric acid and 5 ml of sulfuric acid is added. This mixture is then placed in a water bath at 60°C for 4 hours. 5% potassium permanganate is then added, and the sample is returned to a water bath at 60°C for an additional 30 minutes. It is then cooled and 12% stannous chloride is added. Analysis was performed using a cold vapor atomic absorption spectrometer (Mercury Instrument, VM-3000) (Morgan *et al.*, 1997; Evans *et al.*, 2010). All digested samples were examined thrice against the aqueous standards for Hg.

2.5. Evaluation of Health Risk

2.5.1. Public health risk assessment of m in fish sample

Public health risk assessment of Hg under investigation in tuna samples was determined by calculating the daily intake, weekly intake and target hazard quotient.

2.5.2. Calculation of estimated daily intake (EDI)

The estimated daily intake (EDI) was calculated based on the mean of Hg content of each tuna species. by the following equation:



C is the Hg concentration in fish (mg kg⁻¹ wet weight); FIR is the food ingestion rate, equal to 36 g/person/day for fish and BWa is the reference body weight of 70 kg (Oktariani *et al.*, 2023).

2.5.3. Calculation of estimated weekly intakes (EWIs)

The weekly intakes EWIs was calculated based on the mean of Hg content of each tuna species by the following equation:

 $\mathbf{EWI} = \frac{\mathbf{FIR} \times \mathbf{C} \times \mathbf{7}}{\mathbf{BWa}}.$ (2)

C is the Hg level in fish (mg kg⁻¹ fresh weight); FIR is the food ingestion rate, equal to 36 g/person/day for fish and BWa is the reference body weight of 70 kg (Oktariani *et al.*, 2023). 2.5.4. Calculation of target hazard quotient (THQ)

The target hazard quotient (THQ) is articulated as the ratio between exposure to a toxic element and the reference dose, which represents the maximum level at which no detrimental health effects are anticipated. The reference dose is tailored to the specific trace element under consideration. When the THQ values less than 1, this indicated that, muscle tissue of tuna fish may not cause any serious health risk to the consumers of Libyan. Conversely, if the THQ exceeds 1, there exists a potential for the manifestation of adverse health effects. The estimation of the THQ was conducted utilizing the methodology established by the United States Environmental Protection Agency (US EPA).

 $THQ = \frac{FIR \times ED \times EF \times C}{BWa \times RFD \times ATn} \times 10^{-3}$

In this context, EF denotes the frequency of exposure to the trace element (365 days/year); Ed signifies the exposure duration (70 years). FIR represents the food ingestion rate measured in grams per day for the pertinent food item. C indicates the concentration in wet weight of the trace element within the specified food item; RfD corresponds to the oral reference dose of the trace element 0.0016 (mg/kg bw/day). BWa refers to the reference body weight of 70 kg, and ATn constitutes the averaged exposure time (365 days multiplied by 70 years), with 10^{-3} serving as the unit conversion factor (Antoine *et al.*, 2017; Mohamed *et al.*, 2023).

2.5.5. Statistical analysis

All data are presented as mean values \pm SD, minimum, and maximum derived from three independent experiments. Statistical analysis was performed with SPSS software (Version 25.0). Excel program was used to create graphs.

العدد الحادي عشر مارس March 2025 المجلد الثاني



3. Results and discussion

3.1. Mercury concentration in tuna fish

Understanding the toxic levels in fishes are very significant for regulating human and environmental safety, however, the migrating nature of fishes and the consequent variation in the duration of metal exposure make the process of gauging the toxic levels, quite a complicated task. Nevertheless, there is a considerable variation of individual tolerance of fish to metals, and many other ecological factors, affect metal toxicity (Moiseenko *et al.*, 2001). Among the different aquatic organisms, fishes are probably the

most mobile creatures and are capable of traveling a long distance (Ip et al., 2005).

3.1.1. Mercury concentration in canned tuna samples

All results from analysis of canned tuna fish samples were consistent with the limits set by the (WHO and FAO 2009). The minimum recorded concentration was 0.01 mg/kg wet weight, while the maximum concentration was 0.41 mg/kg wet weight. The calculated mean was 0.12 mg/kg wet weight, and the standard deviation was 0.12 mg/kg wet weight, as shown in Table (1) and Figure (2). From the literature, a research conducted by Abolghait and Garbaj (2015), examined Hg concentration in canned yellow fin tuna samples purchased from the Libyan market, the average Hg concentration was $0.16 \pm$ 0.12 mg/kg wet weight. This is consistent with another research study conducted by Rodriguez-Mendivil et al., (2019), on samples of canned tuna from Mexican markets. The results indicated that Hg concentrations in the wet weight of canned tuna ranged between 0.005 mg/kg and 1.17 mg/kg wet weight. Another study was conducted by Sharkawy et al., (2020), were forty samples of canned tuna collected from five brands from supermarkets in Assiut, Egypt were tested for Hg concentrations, the results were (6.39–6.81), (5.04–5.17), (6.61–7.04), (2.62–3.28), and (1.30–2.19) mg/kg wet weight, the results were higher than the results of this study. Another research was conducted by Miedico et al., (2020), A total of 108 tuna samples, both canned and unprocessed. The mean Hg concentrations in canned tuna were 0.21 (0.18) mg kg⁻¹, these findings were consistent with current study. One more study was conducted by Hanis et al., (2023), the results showed the maximum Hg level in the examined tuna samples was 0.099 mg/kg. this result was at same range of the current research.

العدد الحادي عشر مارس March 2025 المجلد الثاني





Table (1): Mercury results in tuna (canned, frozen and fresh) (mg/Kg w.w)

Fig. (2): Mercury concentration in canned tuna (mg/kg wet weight) 3.1.2. Mercury concentration in frozen tuna samples

Three out of five frozen tuna samples showed levels exceeding the limits recommended by (WHO and FAO 2009). The lowest recorded concentration was 0.19 mg/kg wet weight, and the highest concentration was 2.33 mg/kg wet weight, significantly exceeding the limits proposed by (WHO and FAO 2009). The average concentrations of the samples were 1.02 mg/kg wet weight, accompanied by a standard deviation of 0.87 mg/kg wet weight, as shown in Table (1) and Figure (3). From the literature, similar results were investigated by the results obtained were slightly higher than those reported by Ziarati et al., (2017). Between October 2015 and June 2016, 150 samples of packed frozen fish were randomly collected from prestigious supermarkets in Tehran Province, Iran. The average Hg concentration in fish samples was $0.79 \pm 0.11 \, \mu g/g$, indicating that the average Hg concentration in the frozen fish analyzed in a study from the Arabian Gulf exceeded 0.5 µg/g, the maximum permissible limit recommended by the Joint FAO/WHO Expert Committee on Food Additives (JECFA). In a study conducted by Al-Masry and Rahma (2013) to examine processed meat imported into Syria, results from frozen fish produced from Lake Qatina were higher than the permissible limits set by (WHO and FAO 2009), with a Hg concentration in wet weight of 5.2 mg/kg.

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Fig. (3): Mercury concentration in frozen tuna (mg/Kg wet weight)

3.1.3. Mercury concentration in fresh tuna

All fresh tuna samples results adhered to the limits set by (WHO and FAW 2009). Only one sample exceeded the permissible limits, recording a value of 0.51 mg/kg wet weight, while the lowest concentration was recorded at 0.02 mg/kg wet weight. The mean concentration was determined to be 0.19 mg/kg wet weight, and the standard deviation was 0.12 mg/kg wet weight, as shown in Table (1) and Figure (4). Species of tuna fish (Thunnus spp.) and other large fish species have naturally high concentrations of mercury due to bioaccumulation and their position in the food chain. From the literature results of this study were lower than those reported by Abolghait and Garbaj (2015), were a small samples of fresh tuna taken from the Libyan market. It was observed that the average Hg concentration in small fresh tuna samples was (1.19 ± 0.97) mg/kg wet weight. Furthermore, the finding of this study were lower than those conducted by Rodriguez-Mendivil et al., (2019), which focused on 20 samples of different fish species available in Tijuana, Mexico were the results showed that Hg concentrations of fresh fish samples ranged between 0.14 and 2.14 mg/kg wet weight. Another study conducted by Al-Kazaghly et al., (2025), it was found that the Hg concentration in blue fin tuna (Euthynnus alletteratus) reached of $0.298 \pm 0.061 \,\mu\text{g/g}$ wet weight. As a matter of fact, it has been acknowledged that, generally the accumulation of heavy metals in fishes are administered by various factors including, distinct ingestion, cleansing and removal mechanisms, the metabolic rate of organisms and the ecosystem (Canli and Atli, 2003). On the other hand, few other studies have identified the following factors that influence the concentration of toxic metals in fishes: feeding behaviours (Romeoa et al., 1999), environmental demands, metabolic processes, age and, length and weight of fishes, and their feeding routine (Canli and Atli, 2003).

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Fig. (4): Mercury concentration in fresh tuna (mg/Kg wet weight)

3.1.4. Evaluation of Health Risk

Risk assessment is the scientific evaluation of the probability of occurrence, and severity of known or potential adverse health effects, resulting from human exposure to food borne hazards (Moiseenko *et al.*, 2001). Since seafood is one of the most important food sources in Libya, intake of heavy metals from seafood, especially, toxic elements, is of great concern for human health risk. The mean concentrations of heavy metal in fish muscles were used for this assessment, because it is the edible part of the fish. One of the major purposes of this present study was to identify and quantify the potentially Hg in the muscle tissues of tuna fish species, collected from Tripoli, consequently, perform a risk assessment, to determine, whether the consumption of these fish from these areas, poses health issues to the consumers. Determining dietary intake levels of these substances, which must meet established safety limits, is a key component in assessing the potential health risks posed by hazardous chemicals in food. Table (2) shows the calculated Target Daily Intake (EDI), Target Weekly Intake (EWI), and Target Hazard quotient (THQ) for Hg in tuna.

3.1.5. Weekly intakes (EWIs)

Estimates of weekly Hg intake were derived from analyses of canned, frozen, and fresh tuna and compared to the Provisional Tolerable Weekly Intake (PTWI = 0.025 mg/kg/week body weight) (Olgunoglu *et al.*, 2025). All samples were not exceeded the Provisional Tolerable Weekly Intake (PTWI). In a study conducted by El-Senousi *et al.* (2025) to determine the estimated daily and weekly consumption of potentially toxic elements in (milligrams per day/week) in the five most popular canned tuna varieties on the Egyptian market, the total daily or weekly mercury consumption was below the maximum permissible limit according to (European Commission, 2006; FAO, 2006; WHO, 2008).

العدد الحادي عشر مارس March 2025 المجلد الثاني



3.1.6. Target hazard quotient (THQ)

The target hazard quotient (THQ) for Hg levels in canned, frozen, and fresh tuna was calculated to be less than 1 (table 2), indicating no potential health risks to the Libyan population in studied area after consuming canned, frozen, or fresh tuna. A THQ of less than or equal to 1 indicates no significant health risk; in contrast, a THQ greater than 1 indicates a health problem (Okbah *et al.*, 2014). In a study conducted by Olgunoglu *et al.*, (2025), THQ values in female scorpionfish approached 1, reaching 0.7 during the summer months, indicating a potential increased risk during this period. Stamatis *et al.*, (2019) reported THQ values for Hg exceeding 1 in white tuna (*Thunnus alalunga*) from the North Aegean Sampling Station Area (NASSA) and the Southeastern Aegean sampling station Area (SASSA) in Greece, with ranges of 1.34–5.04, and 0.76–4.05 (mg/kg wet weight), respectively. Another study conducted by Traven *et al.* (2023), showed that, the THQ levels for Hg were less than 1 in the analyzed species. However, the risk of health effects is increased due to the presence of Hg in seafood. Therefore, we recommend that groups most at risk, including young children, the elderly, and pregnant women, limit their consumption of certain types of seafood, especially tuna.

Table (2): Estimated daily intake (EDI), Estimated weekly intake (EWI) of Hg and target hazar
quotient (THQ) in muscles of (canned, frozen and fresh) tuna fish

Sample tuna	Mean	(SD)	EDI (mg/kg b.w/day)	EWI (mg /kg b.w /week)	THQ
Canned	(0.01- 0.41)	0.12	6.15 x 10 ⁻⁵	4.3 x 10 ⁻⁴	3.84×10^{-2}
Frozen	(0.19- 2.33)	0.87	5.24×10^{-4}	3.67×10^{-3}	3.28×10^{-1}
Fresh	(0.02- 0.51)	0.12	9.6 x 10 ⁻⁵	6.72×10^{-4}	6.00×10^{-2}

4. Conclusion

The analysis of results showed that, the concentrations of Hg in most of tuna fish samples were within the permissible limits for canned tuna, except one sample of fresh tuna exceeded the permissible limits, and high readings exceeding four times the permissible limits were recorded in frozen tuna. Contamination may be linked to multiple sources, particularly natural and anthropogenic. A THQ levels for Hg were less than 1 in all the species analyzed indicates no significant health risk to the consumers of Libyan. However, the risk of health effects is increased due to the presence of Hg in seafood. Therefore, we recommend that groups most at risk, including young children, the elderly, and pregnant women, limit their consumption of certain types of seafood, especially tuna. further comprehensive monitoring programs should be conducted.



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العدد الحادي عشر مارس March 2025 المجلد الثاني



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