



## Analysis of Mercury Content in Canned Tuna Fish Commercially Available in the Philippines

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### Abstract

**Objective:** To analyze the total concentration (in mg/kg) of Mercury in Canned Tuna Fish commercially available in the Philippines, using Cold Vapor Atomic Absorption Spectrophotometry (CVAAS) and to compare the results gathered with permissible FAO/WHO levels. **Background:** The levels of the toxic heavy metal, mercury have not been previously determined in canned Tuna commercially available in the Philippines. **Methods:** Six different brands of canned tuna, commercially and widely available in the Philippines were selected. The samples were primed, then analyzed using Cold Vapor Atomic Absorption Spectrophotometry. The values obtained were then compared the tolerable weekly limit of Mercury as set by WHO. **Results:** Of the six canned tuna, all were tested positive for mercury. The mercury content expressed in mg/kg body weight were 0.10, 0.04, 0.06, 0.02, 0.02, and 0.02, for samples A, B, C, D, E and F respectively. The Provisional Tolerable Weekly intake of total mercury is 0.004 mg/kg, as set by the Food and Agriculture Organization/World Health Organization Joint Expert Committee on Food Additives [1]. The recovered mercury from all the canned tunas tested were well above the Provisional Tolerable Weekly Intake of total Mercury [1]. **Conclusion:** All of the 6 cans of tuna samples tested were positive for mercury well above the permissible FAO/WHO levels for mercury. Therefore, the analysis of the canned tuna is considered significant and the canned tuna fish seem to be unsafe for human consumption.

**Keywords:** Canned tuna, Philippines, Cold vapor atomic absorption spectrophotometry, Provisional tolerable weekly intake, Total mercury.

### Contents

1. Introduction .....	58
2. Methods.....	59
3. Results .....	60
4. Discussion.....	60
5. Conclusion.....	60
References .....	61

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## 1. Introduction

Tuna is a globally renowned commercial fish and is widely considered to be a healthy fish to consume. Health benefits included being a rich source of protein and an excellent source of omega-3 fatty acids containing over 200 milligrams per 3 ounce serving [2]. Omega-3 fatty acids in return can increase high-density lipids aka good cholesterol and play a significant role in preventing heart attacks [3]. Tuna is considered an oily fish containing large amounts of vitamin D. It is relatively inexpensive and can easily be prepared.

In the Philippines, popular fishing grounds for tuna include the Sulu Sea, Moro Gulf, waters extending to the North Celebes Sea, Western Negros, as well as Northwestern and Southern Luzon [4]. At present, the Philippines is said to be the world's second exporters of canned tuna. Exporting it averages to 6 million cases of canned tuna with a total worth of \$100 million [5].

The Agency for Toxic Substances and Disease Registry (ATSDR), ranks mercury as third, in the 2007 CERCLA Priority List of Hazardous Substances, which gives a hierarchy of different substances based on their individual potential to cause significant threat to human health along with their known or suspected toxicity and potential risk for human exposure.

Mercury (Hg) is a naturally occurring metal [6]. It is found primarily in the mercury sulfate form aka cinnabar that is released through the natural weathering of rock and (or) volcanic activity [6]. The main source of mercury in the environment is a result of various human activities including but not limited to combustion of fossil fuels especially coal, electric power stations, gold and mercury mining, cement manufacturing, chlorine, pesticides, caustic soda, medical equipment and mirrors, dentistry, industrial leaks and waste and corpse incineration [7]; [8]. A common scenario in the Philippines is polluted fresh water resources such as those in paddy fields that are irrigated with mercury containing tailing sediments [9]. Mercury once released to the environment, tends to persist and cycle globally. Mercury has a global impact on fishing and can generate more significant problems in less developed regions [10]. However interventions may be successful [10]. Fishes are considered to be the single largest source of mercury for humans with the exception of occupational exposure [11]. It was established that cooking cannot significantly decrease the mercury concentration in fish [12]. In general, heavy metals pose the most important risk of pollution in the aquatic biodome due to their toxicity and accumulation among the diverse marine habitat [13]. The biotransformation of mercury along with the formation of methyl mercury creates a perilous problem for human health [14]. Mercury can be converted by bacteria into methyl mercury (MeHg) in streams, lakes and oceans [12]. This accounts for the most prevalent form of organic mercury and the most dangerous form [12]. Methyl mercury largely constitutes more than 90% of total mercury, which is archetypical for a diverse marine environment in the absence of vital point sources [15]. Methylation of mercury is of great concern due to the fact that it is absorbed quite readily along the food chain [16]. Methyl mercury can easily cross biological membrane barriers and can accumulate to dangerous concentrations in the exposed organism. This leads to an increasing bio-magnification along the food chain and can cause high levels of mercury in top predator fishes posing a detrimental effect on humans and fish-eating wildlife [17].

Amid these fishes are tuna which are typically processed, preserved and marketed in cans. There was no apparent effect of the packing medium, species or sample age on the methyl mercury percentages [18]. Tuna is acknowledged as a predator fish capable of concentrating huge amounts of heavy metals. A large number of tuna are used to detect environmental contamination and biomonitoring [13]. Aside from the hazards of environmental pollution, the canning process itself contributes to contamination by heavy metals. Ingestion of food is an evident means of exposure to metals, not only because many metals are natural components of food stuffs, but also through environmental contamination and contamination during processing [19].

Amongst the experimental animal varieties that were analyzed, methyl mercury exhibited up to 95% absorption after oral exposure. Methyl mercury can effectively cross both the blood-brain barrier and the placenta resulting in greater concentrations of mercury in the fetal brain than of the mother. The elimination of methyl mercury is primarily through the bile and feces; with neonatal animals having a lower excretory capability than adults. Methyl mercury is prone to toxicity in multiple organ systems including the nervous system, liver, kidney, and organs of reproduction with neurotoxicity being the most profound [20]. MeHg hinders neurodevelopment by attaching to crucial structures such as microtubules that play a key role in normal cell division and migration. It also adheres to and alters principle molecules like DNA and RNA [21]. The most crucial period of susceptibility is during prenatal period since transplacental exposure theoretically poses the greatest risk [22]. Small quantities of methyl mercury can be transferred by breast milk; however, this is not as sufficient an amount to offset the numerous benefits of breastfeeding. When children start eating solid foods, dietary exposure from fish remain to be a potentially hazard during postnatal neurodevelopment [23]. All forms of mercury are relatively hazardous to humans because it is broadly disseminated in the body and numerous systems are affected. The toxicities of mercury include but not limited to nephrotoxicity, neurotoxicity, teratogenicity and cardiovascular toxicity (elevated risk of hypertension and heart attack) [24]. Methyl mercury has a group 2B classification by the International Agency for Research on Cancer (IARC), i.e. a possible human carcinogen. However, no clear evidence is established regarding its mutagenicity or its consequences on reproduction. Its immunotoxic potential still remain under scientific investigation. Studies have shown that low-level, long-term exposures have been associated with more subtle symptoms of erethism, including irritability, fatigue, vivid dreams, loss of memory, and depression [25]. Severe mercury poisoning is notorious in the development of Minamata disease.

It was noticed that exposure to methyl mercury that is released into the atmosphere by American electric generator plants across the US causes lifelong detrimental loss of intelligence in many American babies born each year [26]. This loss of brainpower significantly costs the country an economic loss totaling to at least hundreds of million dollars each year [26]. A policy was adopted by the American Medical Association that entailed physicians to focus on educating their patients to be more aware of the potential dangers of tuna consumption, especially during pregnancy [27].

The emergent interest of the quality of food has been subjected to many researches. According to a new study by University of Nevada, Las Vegas, more than half of canned tuna samples from a local grocery store failed to meet the strict Environmental Protection Agency safety level for mercury in fish [28]. The FDA only tests about a dozen cans of Albacore tuna for mercury a year and doesn't ask to review the tuna industry's own tests. A recent study conducted among a consumer group showed that as many as 22 million cans of tuna could have potentially high mercury content well above the FDA's approved level, enabling them to be a subject to recall.

The Provisional Tolerable Weekly Intake (PTWI) estimates the amount of a contaminant that can be consumed over a lifetime without significant risk. A consumption above the PTWI does not automatically entail that health is in danger. Transient jaunts above the PTWI would have no health significance if the average consumption over an extended time-frame is not exceeded as the emphasis of PTWI is a lifetime exposure. The PTWI of total mercury for food, as recommended by the Joint FAO/WHO Expert Committee on Food Additives is 0.004  $\mu\text{g/g}$  body weight [1]. A tolerable intake of 0.0016  $\mu\text{g/g}$  bodyweight per week for methyl mercury was instituted, in order to shield the developing fetus from neurotoxic harm. The PTWI of 0.0016  $\mu\text{g/g}$  applies also to children (up to about 17 years). For adults, with the exception of women of childbearing age (to protect the embryo and fetus), up to around two times the tolerable intake per week would not entail any potential of neurotoxicity [29].

The Codex Committee on Food Additives and Contaminants noted that examination of total mercury was generally adequate to warrant that Guideline Levels for methyl mercury were not surpassed. Enforcement can be performed by analysis of total mercury as a screening method (for facilitating control/monitoring). Methyl mercury needs only be determined for verification purposes.

Since canned tuna fish is frequently eaten by a diverse group of people their toxic metal content should be of great concern to human health. The researchers formulated this study in view of the scarcity of information about mercury content in commercially available canned tuna, in hope that the results may give an insight to the possible potential risks of consumption. The data may be of great interest to consumers and advocates of health who are concerned about the presence of toxins or contaminants in the food they eat and their associated health risks. It also stresses the need for a long-term monitoring program to ensure the safety of tuna consumed.

## 2. Methods

### 2.1. Study Design

An experimental method of research was conducted to determine the concentration of mercury in the canned tuna samples.

### 2.2. Research Organization and Procedure

#### 2.2.1. Collection of Canned Tuna Samples

Six brands of canned tuna that were commercially and widely available in the Philippines were selected.

#### 2.2.2. Inclusion and Exclusion Criteria

Inclusion criteria for the tuna samples are: (a) Canned tuna that are widely and commercially available in the Philippines; (b) Tuna flakes in oil as indicated on the label; (c) Must be originally contained and distributed in undamaged tin cans; and (d) must not be expired.

Exclusion criteria for the tuna samples are: (a) Canned tuna that are not commercially available in the Philippines; (b) Variants of canned tuna other than that in oil as indicated on the label; (c) Damaged tin can containers; (d) Expired canned tuna.

Two samples each, of the 6 brands, in their original, unopened tin can packaging, devoid of their brand labels, were labeled as A, B, C, D, E, and F in no specific order, and then sent for analysis at the Philippine Institute of Pure and Applied Chemistry, Ateneo de Manila University, Quezon City.

#### 2.2.3. Preparation of Canned Tuna Samples for AAS

Six brands of canned tuna were used for this study. Each can's content was homogenized in a blender. The sample was then subjected to Acid digestion as follows: the homogenized sample ( $2 \pm 0.001$  grams) was weighed into a 0.5 L glass digestion tube. 10 ml of conc. Nitric Acid and 5 ml of conc. Sulfuric acid were added slowly. The tube was then placed in a steam bath unit to complete dissolution. It was then, cooled and the transferred carefully into a 50 ml volumetric flask. For the reduction of mercury, 5 ml Tin (II) Chloride was used.

#### 2.2.4. Preparation of Standard of the Heavy Metal Mercury

For the calibration of the AAS, three standards were set, as follows: 1.0000 ppm, 1.5000 ppm, and 2.0000 ppm. The absorbance of these standard solutions was measured, and a calibration curve prepared from the obtained values.

#### 2.2.5. Atomic Absorption Spectrophotometric Analysis

Analysis of mercury content in the tuna samples was done using Cold Vapor Atomic Absorption Spectrophotometry (CVAAS), which is a popular technique for determining mercury in a wide variety of samples, and is generally applied to determine total mercury content.

After appropriate adjustments to the spectroscope, the standard and the sample solutions were transferred into the spectroscope, to measure the absorbance of the atomic vapor generated.

Determination was done using the Calibration Curve Method. The absorbance for the sample solution was measured and adjusted in concentration to a measurable range. Finally, the concentration of mercury was determined from the calibration curve.

### 2.2.6. Data Assessment

Data yielded from all the trials were organized in tables. The concentrations in micrograms per gram ( $\mu\text{g/g}$ ), of tuna samples that showed positive results for the presence of mercury were converted into milligrams per kilogram ( $\text{mg/kg}$ ), and then compared to the Provisional Tolerable Weekly Intake limit of total mercury, as set by the Food and Agriculture Organization/World Health Organization Joint Expert Committee on Food Additives (JECFA). These values were then assessed as being greater than or within the tolerable weekly limit of Mercury. This study did not employ any statistical analysis.

## 3. Results

6 samples of canned tuna fish were analyzed for mercury, using the CVAAS, with two replicates for each sample. The data obtained, are presented in Table 1.

Table 2 shows the comparison between Mercury content of the samples and the provisional tolerable weekly intake for Mercury as set by the Food and Agriculture Organization/World Health Organization Joint Expert Committee on Food Additives (JECFA).

Table-1. AAS readings in  $\mu\text{g/g}$

Sample codes	Replicate 1	Replicate 2	Average
A	0.096	0.104	0.10
B	0.039	0.040	0.04
C	0.049	0.065	0.06
D	0.022	0.023	0.02
E	0.023	0.024	0.02
F	0.023	0.024	0.02

The results revealed that all the canned tuna samples, namely A, B, C, D, E, and F, were positive for Mercury, with average concentrations of 0.10, 0.04, 0.06, 0.02, 0.02 and 0.02 respectively.

Table-2. Comparison between Provisional Tolerable Weekly Intake of Total Mercury and Actual Concentrations from Canned Tuna Samples  
\*1  $\text{mg/kg} = 1 \mu\text{g/g}$

Sample Codes	Concentration ( $\mu\text{g/g}$ )	Concentration ( $\text{mg/kg}$ body weight)*	Maximum allowable limit for Mercury ( $\text{mg/kg}$ body weight)
A	0.10	0.10	0.004
B	0.04	0.04	0.004
C	0.06	0.06	0.004
D	0.02	0.02	0.004
E	0.02	0.02	0.004
F	0.02	0.02	0.004

The PTWI of total Mercury is 0.004  $\text{mg/kg}$ . However, all the samples had concentrations of Mercury, well above the Provisional Tolerable Weekly intake as set by WHO and JECFA.

## 4. Discussion

The presence of mercury in the canned tunas, well above the PTWI specifies that the mercury content surpasses the limit that may be consumed over a lifetime without significant risk. Thus, there exists probable health risks of consumption, and it has a prominent impact to the chemical body burden. An intake above the PTWI does not automatically entail that health is at peril. Transitory excursion beyond the PTWI would have no health concern if the mean consumption over an extended period is not surpassed as the emphasis of PTWI is a lifetime exposure. However, since only the total mercury content was analyzed, supplementary research is essential to evaluate the specific methylmercury level and to establish a clear-cut view of the degree of health threat. The results of this study probes for reassessment by the government regulatory agency, product manufacturers, distributors, health professionals and consumers. It also emphasizes the need for greater efforts to ensure a mercury free environment, including health care facilities (~5% of all Hg water releases) and other inadvertent or intentional anthropogenic sources. This study contributes to the awareness of the environmental occurrence of mercury and the way they may reach the developing human organism, facilitating the formulation of fish consumption guidelines, especially for women of child bearing age and children.

Also, notable, is the likelihood that MeHg content transcends to the level required to protect the developing fetus. The Half-life of Mercury in adults is 45-70 days—Therefore, prospective mothers can significantly reduce mercury body burden by avoiding exposure for 6-12 months prior to pregnancy. In addition it calls the need for long-term monitoring programs to ensure the safety of tuna consumed.

## 5. Conclusion

Though estimates of the amount of mercury consumed in the diet are difficult to obtain and a discussion of metal tolerances in the diet is beyond the scope of this paper, it can be concluded from the results so far obtained that mercury content of the canned tuna fish commercially available in the Philippines is above the permissible FAO/WHO levels for mercury and is thus likely to constitute significant health hazard, especially to the vulnerable segments of the population- fetus, infants, young children and women of child bearing age.

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