



Heavy Metals in Canned Fish Marketed in Accra

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ABSTRACT

Heavy metal (Cd, Sn, Hg and Pb) concentrations of canned fish sold on markets in Accra were determined using Atomic Absorption Spectroscopic (AAS) procedures. Levels of cadmium (Cd), tin (Sn) and lead (Pb) were determined by graphite furnace atomic absorption spectrometry (GF-AAS). Mercury (Hg) content was analysed by the cold vapour atomic absorption spectroscopic technique after Hg ions reduction with SnCl₂ (CV-AAS). The accuracy of the method was determined by use of a certified reference material (DORM-2 (Dogfish muscle)). The average contents of heavy metals in canned fish brands were found as 10.03 mg/kg for tin, 0.11 mg/kg for cadmium, 0.203 mg/kg for lead, and 0.04 mg/kg for mercury. Although these products pose no risk with respect to the concentrations of tin and mercury, some of the samples had contents of lead and cadmium higher than the acceptable limits. Comprehensive and intermittent monitoring of heavy metals in canned fish is needed to assess the safety of these products with respect to human health.

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Introduction

The most essential feature of fish meal is its advantageous fatty acid profile, resulting from the consistent content of essential polyunsaturated fatty acids, such as eicosapentaenoic and docosahexaenoic acid, known to support good health (Usydu *et al.*, 2009). It is estimated that the consumption of one portion of fatty fish, daily, brings about 900 mg/day of n-3 acids, with consequent decline of mortality in patients with coronary diseases. However, the incontrovertible benefits derived by fish consumption may be offset by the presence of toxic metals, such as Cd, Pb and especially Hg, which is present in many fish species often at levels exceeding the safety standards established by legislation of various countries (Kris-Etherton *et al.*, 2002). Heavy metals have attracted a great deal of global attention from regulatory and other government agencies who are concerned with reducing the human health risk associated with environmental pollution. Heavy metals are considered as one of the most important form of pollution of the aquatic environment because of their toxicity and accumulation by marine organisms. The main exposure by humans to these heavy metals (Hg, Cd, Pb and Sn) is through the ingestion of contaminated fish, especially larger predators. While mercury, arsenic, cadmium and lead can be tolerated at extremely low concentrations, they are extremely toxic to humans. Though tin is widely used for studding in canning, its toxicity is not as imperative as other heavy metals.

These pelagic organisms are high performance fish with very high metabolic rates thus, high food intake rates, a property that accentuates the exposure to trace elements (Kojadinovic *et al.*, 2007). As a result, human health may be adversely affected if fish is consumed too often or in large quantities. It is imperative to consider canned tuna, which undoubtedly is the most consumed-canned fish product because of its convenience

and affordability for most working families. Nevertheless, published data on the concentrations of toxic elements in canned tuna and dietary intakes of these elements via these fishery products in Ghana are lacking. Tuna, as a predator, is able to concentrate large amount of heavy metals. Some of them are used for biomonitoring of environmental contamination (Enomoto & Uchida, 1973; Schmitt & Brumbaugh, 1990). Canned tunas are a popular food source in Ghana, so their toxic metal content should be of concern to human health.

The distribution of metals varies between fish species, depending on age, development status and other physiological factors (Kagi & Schaffer, 1998). Fish accumulate substantial concentrations of mercury in their tissues and thus can represent a major dietary source of this element for humans. Mercury is a known human toxicant and the primary source of mercury contamination in man is through eating fish. Biotransformation of mercury and methyl mercury formation constitutes a dangerous problem for human health (Inskip & Piotrowski, 1985).

Metal contaminations in food, especially in marine products, have been broadly investigated (Catsiki & Stroglyoudi, 1999; Enomoto & Uchida, 1973; Glover, 1979; Liang, Cheung, & Wong, 1999; Martin De La Hinojosa, Hitos Natera, Cerrezo Rubio, & Reyes, 1995; Uysal, 1980; Uysal, 1990). The present study was, therefore, carried out in view of the paucity of information about heavy metals in canned products. It is hoped that the results of this study will help in generating data needed for the assessment of toxic metal intake from this food source. The objective of the study was to determine the concentration of Hg, Pb, Cd and Sn in canned fish products purchased from supermarkets located in the Accra Metropolis relative to the maximum levels established by the European Union Legislation.

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Materials and methods

Collection of Samples

Fifteen (15) popular brands (three lots of each brand) were purchased in large supermarkets and grocery stores in Accra.

Apparatus

All glassware were soaked overnight in 10% (v/v) nitric acid, followed by washing with 10% (v/v) hydrochloric acid. It was rinsed with double distilled water and dried before using.

Reagents

All the reagents and chemicals used were of analytical grade Merck (Darmstadt, Germany) but concentrated 65% HNO₃ and 30% H₂O₂ were of spectroscopic grades. Standard solutions of heavy metals (1000 mg/l) namely, mercury (Hg), lead (Pb), tin (Sn) and cadmium (Cd), were procured from Aldrich. The standards were prepared from the individual 1000mg/L standards (Merck), in 0.1 N HNO₃. Stock standard solution of chemical modifiers, Mg (NO₃)₂ (2.00 gL⁻¹), was prepared from Mg (NO₃)₂ (Merck) and Pd stock standard solution (3.00 gL⁻¹), was prepared from Pd 99.999%.

Sample preparation and digestion

Fifteen cans of tuna (about 2 kg each) were used for this study. After opening each can, oil was drained off and the meat was homogenized thoroughly in a food blender with stainless steel cutters. The samples were then taken and digested promptly as follows: the homogenized sample (0.5 ± 0.001 g) was weighed into vessels of the microwave digester (MA079) with 4ml and 2ml of HNO₃ and H₂O₂ respectively. The required parameters were entered for the operation of the microwave digester-. The digest were transferred into marked or graduated flask and diluted to the 20ml mark with deionized water after rinsing the walls of the vessel into it. Cadmium (Cd), tin (Sn), and lead (Pb) were determined by graphite furnace atomic absorption spectrometry (GF-AAS), equipped with a deuterium background corrector. Mercury (Hg) content was analysed by using the cold vapour atomic absorption technique after Hg ions reduction with SnCl₂ (CV-AAS).

Quality Control

The quantification was performed using a calibration curve of the corresponding standards. Triplicate analyses were performed for each sample. Accuracy was evaluated by certified reference material for trace metals, DORM-2 (Dogfish muscle), was purchased from the National Research Council Canada (Ottawa, Ontario, Canada). The results were found within ± 5% of the certified values.

Deionized water was obtained from a Pure Lab Classic machine. Blanks and calibration standard solutions were similarly analysed as the digested sample solution, and calibration curves constructed.

Results and Discussion

Table 1.0 shows the levels of Hg, Sn, Cd and Pb in fifteen (15) canned fish brands collected from markets in Accra.

| Sample | Hg | Sn | Cd | Pb |
|--------|------|-------|------|------|
| A | 0.01 | 18.32 | 0.09 | 0.24 |
| B | 0.01 | 19.66 | 0.06 | 0.24 |
| C | 0.03 | 8.57 | 0.03 | 0.19 |
| D | 0.01 | 16.96 | 0.13 | 0.22 |
| E | 0.02 | 6.79 | 0.04 | 0.26 |
| F | 0.02 | 17.42 | 0.34 | 0.32 |
| G | 0.04 | 11.2 | 0.16 | 0.18 |
| H | 0.04 | 29.21 | 0.06 | 0.12 |
| I | 0.09 | 13.35 | 0.08 | 0.17 |
| J | 0.01 | 8.97 | 0.07 | 0.17 |
| K | 0.03 | 0 | 0.46 | 0.11 |
| L | 0.04 | 0 | 0.06 | 0.23 |
| M | 0.01 | 0 | 0.08 | 0 |

| | | | | |
|---|------|---|------|------|
| N | 0.02 | 0 | 0.01 | 0.27 |
| O | 0.15 | 0 | 0.11 | 0.33 |

Table 1.0 Heavy Metals in Canned Fish brands from Markets in Accra

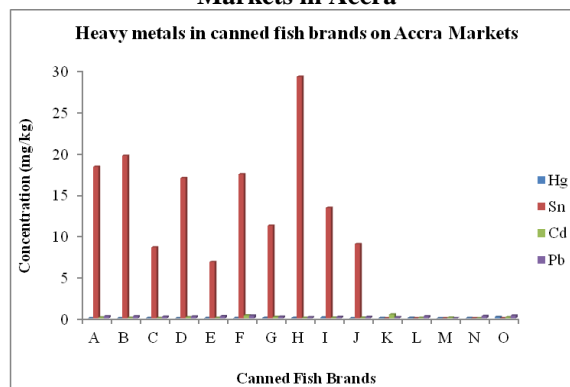


Fig 1.0 Heavy metal concentrations in canned Fish brands from markets in Accra

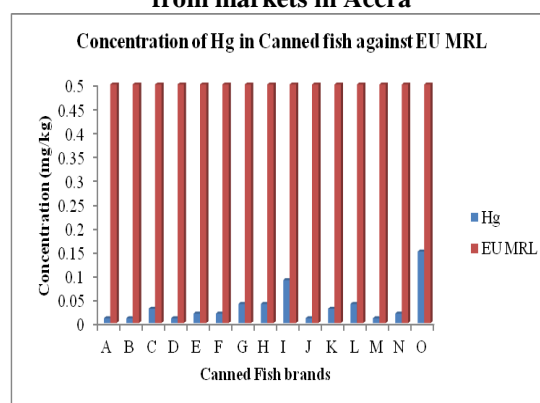


Fig 2.0 Concentration of Hg in canned Fish brands against EU MRL

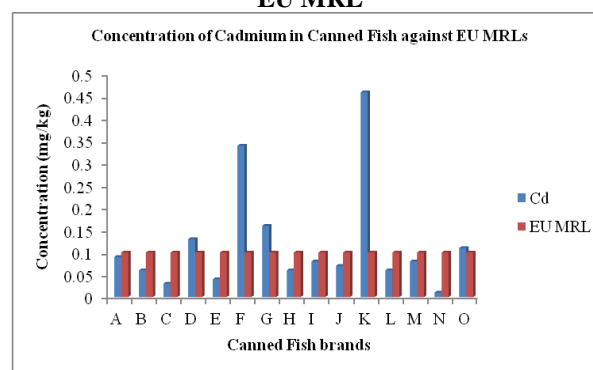


Fig 3.0 Concentration of Cd in canned Fish brands against EU MRL

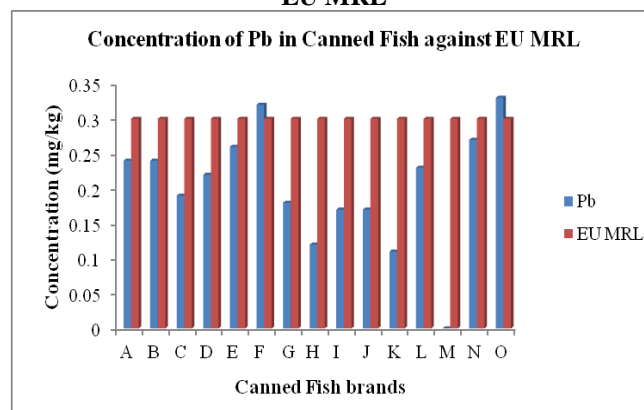


Fig 4.0 Concentration of Pb in canned Fish brands against EU MRL

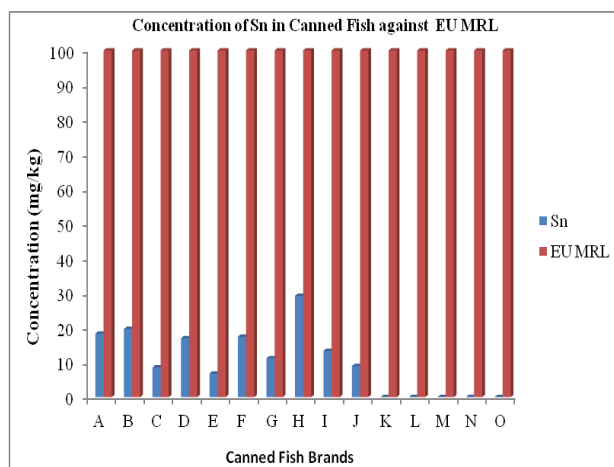


Fig 5.0 Concentration of Sn in canned Fish brands against EU MRL

From table 1.0, Sn (ND–29.1, average: 10.03 mg/kg) had the highest concentration, followed by Cd (0.01–0.46, average: 0.11 mg/kg), Pb (ND–0.33, average: 0.203 mg/kg) and Hg (0.01–0.15, average: 0.04 mg/kg). Among the metals analyzed, Cd and Hg were present in all canned tuna samples, while Sn and Pb were detected in 66.7% and 93% of samples analyzed respectively.

From a more comprehensive analysis of the results, it appeared that Sn and Hg levels were rather low and did not exhibit a wide between-brands variation, whereas the analysis of Cd and Pb contents revealed strong differences in specimen contamination level, suggesting a trend in the tissue residues of these metal based on sample size. Based on the European Union legislation (Official Journal of the European Union (EU), 2006), standard, Cd concentrations exceeds were observed in 33.33% of the samples whereas 13.33% of the samples analyzed exceeded their Pb concentrations.

Cadmium (Cd)

Abou-Arab et al., 1996 states that cadmium may cause symptoms of chronic toxicity, including impaired kidney function, poor reproductive capacity, hypertension, tumours and hepatic dysfunction. Thus, EU (2006) proposed the maximum limit for this metal in fish as 0.1 mg/kg. In this study, Cd contents of 66.7% samples analyzed were below these limits. The highest value was recorded from sample K (0.46 mg/kg) while sample N (0.01 mg/kg) had the least concentration. This result shows the importance of periodical controls of heavy metals in canned fish especially with exceeds. Considering the levels of Cd in the fifteen canned fish samples analyzed, long term exposure may cause nephrotoxicity in humans, mainly due to abnormalities in tubular re-absorption. Cadmium is poorly excreted by the human body and although only 5–10% of the ingested is absorbed, it does accumulate in the body over time with renal damage being caused by long-term exposure (WHO, 1993). One sign of Cd damage is proteinuria (the appearance of increased levels of unaltered proteins in the urine. The major source of cadmium contamination in fish may be from supply of phosphate fertilisers, atmospheric deposition and sewage sludge.

Tin (Sn)

Estimation of Sn in canned food is vital for quality assessment. This is as a result of the fact that, tin content is an indication of the degree of corrosion of the container, therefore affects the suitability of food (Sumitani et al., 1993). The highest Sn concentration in this study was recorded by sample H (29.21mg/kg) where as samples K, L, M, N and O had no

detections for Sn. Tin concentrations were below the permissible limit of 250 mg Sn/kg specified by the European legislation (Official Journal of the European Union, 2006) in all samples. The main source of tin in the canned fish samples is from the tin-plated steel used in the manufacture of cans for foods and beverages. According to the UK's Ministry of Agriculture, Fisheries and Foods Surveillance paper (1998), high tin concentrations in food may cause short-term acute health effects in some people, including stomach upsets, abdominal cramps, nausea and/or diarrhoea. These short-term effects may occur in some individuals at concentrations above 200 mg/kg.

Mercury (Hg)

All the samples were below the acceptable limits proposed of 0.5 mg/kg (EU, 2006). The highest Hg concentration was recorded by sample O (0.15 mg/kg) whereas samples A, B, C, D, J and M (0.01mg/kg) had the least concentrations. In a similar study, Ikem and Egeibor (2005) determined the average values of trace metals in canned fishes from Georgia and Alabama. They reported the average Hg contents as 0.036 mg/kg, and 0.032 mg/kg in canned pink salmon and canned red salmon, respectively. Many studies have also shown that mercury is bioamplified in the food chain. As such high-trophic level predatory species, such as tuna sharks and swordfish, generally have high mercury concentrations. Mercury can cause adverse effects on the renal and nervous systems and can cross the placenta with potential toxic effects on the fetus (Tong *et al.*, 2000).

Lead (Pb)

Lead is a widely distributed environmental poison. For instance, solder used in the manufacture of cans is a source of contamination of food by Pb. Clinical manifestations of Pb toxicity include symptoms referable to the Central nervous system, the peripheral nervous system, the hematopoietic system, the renal system and the gastrointestinal system (Satarug and Moore, 2004). The maximum lead level permitted for canned fish is 0.3 mg/kg by EU legislation (2006). Sample O (0.33mg/kg) recorded the highest concentration of Pb but in sample M none was not detected. All samples had their concentration falling within the specified limits of the EU legislation (2006) with the exception of samples F and O (0.32 and 0.33 mg/kg respectively).

The levels of toxic elements in fish are related to age, sex, season and place (Kagi & Schaffer, 1998). It is also reported that cooking reduces the amount of some metals (Atta, El-Sebaie, Noaman, & Kassab, 1997). Moreover, the advances of new packaging technology, especially the use of cans with lacquered walls and mechanical seam, reduce or, in most cases, eliminate the leaching of heavy metals (lead and tin) into the food. Badsha and Goldspimk (1988) showed that the factors affecting uptake and accumulation of pollutants in fish were locality, sex, species, age and state of gonadal maturation, as well as environmental factors.

Conclusion

The average levels of all metals studied (Sn, Hg, Cd and Pb) were within the levels specified by the EU. It was determined that, these products pose no risk with respect to the concentrations of tin and mercury. Therefore, their contribution to the total body burden can be considered as negligible. However the results also indicated that, some of the canned fish samples analyzed had higher contents of lead and cadmium than the permissible limits. Therefore periodic monitoring of heavy metals in canned fish is needed both for the assessment of toxic

metal intake from these products and for generating data for further studies. The results of the present study suggest the need for an increasing effort in controlling the sources of heavy metal pollution in this area.

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