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Heavy metal contamination in canned fish marketed in Ghana

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ABSTRACT

The concentrations of Pb, Zn, Fe, Cd, Mn and Hg in 46 canned fish samples of nine different brands purchased within Kumasi in the Ashanti Region of Ghana were determined using the Flame Atomic Absorption Spectrophotometer for Pb, Zn, Fe, Cd and Mn and direct mercury analyzer (DMA) for Hg. The ranges obtained for the elements analyzed in $\mu\text{g/g}$ (wet weight) are as follows: Pb (0.058 - 0.168), Zn (0.010 - 0.370), Hg (0.088 - 0.410), Mn (0.001 - 0.057), Fe(0.990 - 32.607) and Cd, below detection limit in all the samples. The fish samples had Hg levels below the European dietary limit of 0.5 $\mu\text{g/g}$. Zinc levels were generally below the Food and Agriculture Organization (FAO) recommended limit of 40 $\mu\text{g/g}$. The concentration of lead in the canned fish was also below the MAFF guidelines of 2.0 $\mu\text{g/g}$. Also, based on the United States Environmental Protection Agency (US EPA) health criteria for carcinogens, there are no health risks associated with Pb concentrations in canned fishes analyzed. The result of the one-way analysis of variance (ANOVA) conducted on the data suggested no significant variations ($P>0:05$) in the concentrations of the metals in the same brands of canned fishes.

Keywords: canned fish, dietary intake, heavy metals, Kumasi, A.A.S, D.M.A.

INTRODUCTION

The toxic nonessential metals— cadmium, mercury, and lead are characterized as having no demonstrated biological requirement in humans, and exposure is associated with recognizable toxicity. Also, severity of toxicity increases with increases in dosage. Although there may be some lower limit of exposure at which toxicity may not be detected (threshold), there may be no level at the molecular level that does not have an adverse effect (Goyer, 1994).

Fish is widely consumed in many parts of the world by humans because it has high protein content, low saturated fat and also contains omega 3 fatty acids known to support good health (US EPA, 2004). Fish is a major source of iron for adults and children. Iron deficiency causes anemia (Institute of Medicine, 2003). The consumption of canned fishes in particular is widespread in the developed world especially in United States of America because it is convenient and affordable for most working families. The latest data from the FAO show that the United States ranks as the third largest consumer of seafood in the world, importing 76% of its seafood (NOAA, 2002). For example, canned tuna is consumed by about 90% of American households and accounts for around 20% of US seafood consumption. Children eat more than twice as much tuna as any other fish,

and canned tuna is also the most frequently consumed fish among women of childbearing age (Mercury Policy Project, 2003). Fish may be contaminated by toxic elements during fish growth, transportation, and storage. Contamination may also occur during production handling and canning process.

Lead poisoning is generally ranked as the most common environmental health hazard (Goyer, 1994). Apart from threat from polluted environment, canned fish is subjected to lead contamination during canning process. Solder used in manufacture of cans has been recognized as a source of lead contamination during canning (MAFF, 1995).

The toxic effects of heavy metals particularly mercury, cadmium and lead have been broadly studied (Uchida *et al.*, 1961; Schroeder, 1965; Venugopal and Luckey, 1975; Inskip & Piotrowski., 1985; Nishihara *et al.*, 1985; Kurieshy & D'siliva., 1993; Narvaes, 2002). Levels of heavy metals in fish have been widely reported (Winchester, 1988; Kowalewska & Korzeniewski, 1991; Sharif *et al.*, 1991; Hossain *et al.*, 1993; Joseph & Srivastava, 1993).

Metal contaminations in food, especially in marine products has also been broadly investigated (Enomoto & Uchida, 1973; Glover, 1979; Uysal,

1980; Uysal, 1990; Liang *et al.*, 1999; Catsiki & Stroglyoudi, 1999). High lead (Edwards *et al.*, 2001) concentrations in fish have also been reported.

The WHO has adopted the US EPA levels for mercury and recommends that food with concentrations of 0.5 mg/kg or more should not be sold for human consumption. In Japan, because of the high consumption of fish, the government has recommended that fish with mercury level of 0.3mg/kg (wet weight) or over should not be sold (Dickman and Leung, 1998). The US FDA currently stipulated an action level of 1.0 mg/kg for methyl mercury in the edible portion of fish pending when all new data are evaluated (FDA, 2000).

Publications on the concentrations of trace elements in processed or canned fishes and dietary intakes of toxic elements from canned fishes in Ghana are limited.

Information on the metal content in canned fish is important to ensure that the fish consumed is safe for human consumption. This study reports the concentrations of heavy metals in canned fish samples purchased from food outlets in the Ashanti region of Ghana.

MATERIALS AND METHODS

Apparatus: All glassware were soaked overnight in 10% (v/v) nitric acid, followed by washing with 10% (v/v) hydrochloric acid, and rinsed with double distilled water and dried before using. Determination of mercury in all the digests was carried out by cold vapour atomic absorption spectrophotometer using an automatic Mercury Analyzer Model HG-5000 (Sanso Seisakusho co., Ltd, Japan) developed at NIMD.

A UNICAM Model 929 flame atomic absorption spectrophotometer equipped with a deuterium background corrector was used for the determination of lead, cadmium, zinc, manganese and iron.

Reagents: All reagents used were of analytical reagent grade. Standard stock solutions of mercury, cadmium, lead, zinc, manganese and iron were prepared from Titrasol (1000 mg/l) (Merck, Germany) and were diluted to the desired concentrations for the corresponding metals. The acids used were purchased from BDH, England. The working solutions were freshly prepared by diluting an appropriate aliquot of the stock solutions using 10% HNO₃ for diluting lead and cadmium solutions, 1 M HCl and 5% H₂SO₄ for diluting mercury solution. Stannous chloride, for mercury analysis, was freshly

prepared by dissolving 10 g in 100 ml of 6 M HCl. The solution was boiled for about 5 min, cooled, and nitrogen bubbled through it to expel any impurities.

Sample preparation and Digestion: Nine different brands of forty six canned fishes (about 0.5 kg each) and their sauces were used for this study. They are labeled AQ₁ (n=5), AQ₂ (n=5), BS (n=7), SM (n=5), LS (n=6), VP (n=5), GM (n=6), PS (n=4) and TS (n=3). After opening, each can content was homogenized thoroughly in a food blender with stainless steel cutters. A sample was then taken and digested promptly as follows: the homogenized sample (2 ± 0.001 g) was weighed into a 0.5 L glass digestion tube, and for mercury, 10 ml of conc. HNO₃/HClO₄ at a ratio of 1:1 and 5 ml of conc. H₂SO₄ were slowly added. The tube was then placed on top of a steam bath unit to complete dissolution. It was then removed from the steam bath, cooled and the solution transferred carefully into a 50 ml volumetric flask.

For the determination of lead, cadmium, zinc, manganese and iron, about 2 ± 0.001 g of homogenized sample was weighed into a 200 ml beaker and 10 ml of conc. HNO₃ was added. The beaker was covered with a watch glass and, after most of the sample had dissolved by standing overnight, heated on a hot plate with boiling until any vigorous reaction had subsided and a clear solution obtained. The solution was allowed to cool, transferred into a 50 ml volumetric flask and diluted to the mark with distilled water.

Chemical analysis: Mercury was determined by Cold Vapor Atomic Absorption Spectrophotometer using the Direct Mercury Analyzer. Lead, cadmium, zinc, manganese and iron, were determined using UNICAM 969 Flame Atomic Absorption Spectrometer. The detection limits in µg/ml for the metals are 0.010 for lead, 0.001 for cadmium, 0.002 for zinc, 0.002 for manganese, 0.005 for iron and 0.001 for mercury.

Quality assurance: The accuracy of the analytical procedure was checked by duplication of the samples and analytical validation was conducted through the analysis of certified reference samples (DORM-2) for mercury and other metals. Method blanks were conducted for all metal determinations in fish samples. The blanks for the elements determined on Flame A.A.S were prepared by following the analytical steps in the analysis method without a sample. Prior to the mercury determinations in fish samples, the mercury levels were first determined by

analyzing them as blanks under the same experimental condition used to analyze the samples. DORM-2 standards were analyzed in between ten sample runs and then followed by the analysis of blank boats prior to commencement of more sample runs.

Statistical Methods: The descriptive statistics (mean and range) and one-way analysis of variance (ANOVA) were conducted using excel software. A one-way ANOVA statistical procedure was employed in the assessment of variation in metal concentrations among canned fish of the same brand and across canned fish of different brands.

RESULTS AND DISCUSSION

Table 1 shows the measured values obtained from the analyses of DORM-2. The data obtained from the analyses of the standards show a strong agreement with the certified reference values provided by the NRC of Canada.

Table 1. Validation of Flame A.A.S and DMA with certified reference material (DORM-2)

| Element | DORM-2 (dogfish muscle) | |
|---------|-------------------------|------------------------|
| | Certified value(mg/kg) | Measured value (mg/kg) |
| Pb | 0.065±0.007 | 0.062±0.004 |
| Zn | 25.6±2.3 | 25.8±0.23 |
| Fe | 142±10 | 143±2.23 |
| Mn | 3.66±0.34 | 3.62±0.12 |
| Hg | 4.64±0.26 | 4.32±0.05 |

The concentrations of lead, zinc, iron, manganese, cadmium and mercury, are presented in Table 2 below with means and ranges. The results indicate that Pb concentration in canned fish ranged from 0.058 - 0.168 µg/g whereas Zn concentration ranged from 0.010 - 0.370µg/g and below detection limits for Cd in the canned fish. Levels of Hg in canned fish ranged from 0.088 - 0.410 µg/g. Fe concentration in the canned fish ranged from 0.990 - 32.607µg/g while Mn concentration in the canned fish ranged from 0.001 - 0.057µg/g. Statistical analysis of the concentrations of each heavy metal by ANOVA showed no significant differences within the samples of the same brand $P > 0.05$.

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 *et al.*, 1997) whereas the concentration of mercury in fish cannot be reduced by cooking.

The concentration of mercury, cadmium, and lead in canned fish from the Mediterranean coast are of the ranges 0.02–6.60, 0.09–0.32 and 0.04–0.18µg/g respectively (Voegborlo, El-Methnani, & Abedin, 1999) and work done in lakes in Tokat, Turkey by Mendil *et al.*, (2005) gave levels of zinc, iron, and lead respectively as 48.6µg/g, 167 µg/g, and 2.8 µg/g. Other surveys by the committee for inland Fisheries of Africa, (CIFA) showed that cadmium levels in several fish types caught in upper Australia waters were 0.10 – 0.13 and 0.050 – 0.97 µg/g (CIFA, 1992). Tuzen and Soylak (2007) reported levels of zinc, iron, lead and cadmium in canned fish marketed in Turkey in the ranges of 0.90-2.50 µg/g, 10.2-30.3 µg/g, 0.09-0.40 µg/g and 0.06-0.25 µg/g respectively. The levels of cadmium obtained in our work were lower than the US-EPA recommended limit of 0.20µg/g. The concentration of lead in all the samples was lower than US-EPA recommended limit of 4.0µg/g. The concentration of mercury in this study, 0.088-0.410µg/g, is lower than that reported in canned fish 0.82 – 1.2µg/g by Holden (1973) and comparable with 0.04 – 0.44 µg/g by Fricke *et al.*, (1979). The metal content in canned tuna fish reported by Khansari *et al.* (2005) varied from 0.0430 – 0.253 for mercury, 0.0046 – 0.0720 for cadmium and from 0.0162 – 0.0726 for lead.

The concentration of mercury, cadmium and lead in canned fish previously reported by FDA (2000) were 0.082 – 0.160, 0.006 – 0.088 and 0.016 – 0.049 µg/g respectively. These results are similar to what was obtained in this research except for lead and mercury which were lower than the results obtained in our work.

The variation of metal concentration in the different canned fish analyzed could be attributed to the fact that some fish are older in age than others. The level of contaminants in fish is influenced by the duration of exposure of fish to contaminants in water, feeding habit of fish, concentrations of contaminants in water column, water chemistry, contamination of fish during handling and processing, quality of canned fish and shelf life of canned fish. According to Taha' n, *et al.* (1995), the pH of the canned product, the quality of the lacquer coatings of canned products, oxygen concentration in the headspace, quality of coating and storage place may also control metal levels in canned fishes. The results obtained for manganese in canned fish studied was comparable with the results obtained by Ikem and Egiebor (2005) which ranged from 0.01 - 2.55µg/g and lower than the

corresponding maximum level reported for canned sardines in Brazil (15.77 µg/g; Tarley *et al.*, 2001).

Table2: Concentration of heavy metals in canned fish (mean and range)

| Sample (Fish and Type) | n | Pb (µg/g) | Zn (µg/g) | Fe (µg/g) | Cd (µg/g) | Mn (µg/g) | Hg (µg/g) |
|----------------------------|---|--------------------------|--------------------------|----------------------------|-----------|--------------------------|--------------------------|
| AQ ₁ (mackerel) | 5 | 0.140 (0.132 – 0.154) | 0.171 (0.168 - 0.185) | 1.930 (1.720- 2.100) | <0.001 | 0.018 (0.017 – 0.019) | 0.102 (0.093 – 0.105) |
| AQ ₂ (mackerel) | 5 | 0.165 (0.163 – 0.168) | 0.068 (0.066- 0.072) | 1.185 (1.135- 1.400) | <0.001 | 0.008 (0.006 - 0.011) | 0.128 (0.127 -0.130) |
| BS (sardine) | 7 | 0.099 (0.058 – 0.152) | 0.136 (0.040 - 0.158) | 9.230 (8.330-10.200) | <0.001 | 0.035 (0.020 – 0.041) | 0.128 (0.120 – 0.145) |
| SM (mackerel) | 5 | 0.125 (0.091 – 0.144) | 0.143 (0.126 - 0.175) | 15.100 (10.400- 17.200) | <0.001 | 0.036 (0.033 – 0.044) | 0.135 (0.088 – 0.163) |
| LS (sardine) | 6 | 0.155 (0.144- 0.158) | 0.155 (0.106 - 0.193) | 21.300 (14.215-32.607) | <0.001 | 0.020 (0.008 - 0.025) | 0.143 (0.140 – 0.146) |
| VP (pilchard) | 5 | 0.136 (0.127 – 0.141) | 0.193 (0.010-0.365) | 11.480 (10.110-16.320) | <0.001 | 0.019 (0.011 – 0.041) | 0.400 (0.399 – 0.410) |
| GM (mackerel) | 6 | 0.136 (0.128- 0.141) | 0.166 (0.043 - 0.370) | 10.900 (10.130-12.204) | <0.001 | 0.006 (0.001- 0.013) | 0.140 (0.135 – 0.142) |
| PS (sardine) | 4 | 0.156 (0.152 – 0.163) | 0.179 (0.138 – 0.217) | 21.450 (14.210- 32.550) | <0.001 | 0.036 (0.022 – 0.057) | 0.141 (0.140 – 0.141) |
| TS (sardine) | 3 | 0.087 (0.086- 0.088) | 0.088 (0.086-0.090) | 1.063 (0.990- 1.200) | <0.001 | 0.006 (0.005 - 0.007) | 0.117 (0.110 – 0.120) |

United States National Research Council has recommended safe and adequate daily intake levels for manganese that range from 0.3 to 1 mg/day for children up to 1 year, 1–2 mg/day for children up to age 10, and 2–5 mg/day for children 10 and older (Institute of Medicine, 2003). Daily intake of small amounts of manganese is needed for growth and good health in children. Children, as well as adults, who lose the ability to remove excess manganese from their bodies, develop nervous system problems. According to the EPA, there is no information on the carcinogenicity of manganese (Agency for Toxic Substances and Disease Registry, 2004).

The Range for iron in muscles of sardines (Canli and Atli, 2003) in µg/g was 39.607±8.62. The results were comparable with some of the concentrations obtained in this work.

Significant variation in the concentrations of lead, mercury, iron, manganese and zinc existed across the various fish species and canned fish brands ($P < 0.05$). However, there were no significant variations ($P > 0.05$) of these metals in the same

species. There was also no significant variation for cadmium across the various fish species and canned fish brands.

CONCLUSION

The metal contents in canned fish, expressed in µg/g wet weight, varied from 0.058 - 0.168 for lead, from 0.010 - 0.370 for zinc, from 0.088 - 0.410 for mercury, from 0.001 - 0.057 for manganese, from 0.990 - 32.607 for iron, and below detection limit for cadmium. The results from this study suggested that significant differences existed in the element concentrations across nine different canned fish brands. Also, analytical data obtained from this study shows that the metal concentrations for the varieties of canned fishes were generally within the WHO/FAO, FDA and US. EPA recommended limits for fish. There is therefore no serious health risk associated with the consumption of canned fishes analyzed. Both low-risk groups (adolescents and adults) and high-risk groups (pregnant mothers and children) must, based on the results obtained, reduce the consumption of canned fish as frequent

consumption may result in bioaccumulation of the metals and increased health risks. Globally, further reduction in the levels of environmental contaminants emanating from power plants and other industrial emissions and effluent discharges are highly needed to reduce contaminant inputs into the aquatic environment. More research and assessments of seafood quality is needed in many countries to provide more data and help safeguard the health of humans.

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