Total Levels of Mercury Concentrations in Marine Fish - Kumasi, Ghana

Charles Afriyie-Debrah\textsuperscript{1,2*}, Priscilla Francisco Ribeiro\textsuperscript{1} and David Baah\textsuperscript{2}

\textsuperscript{1}Biotechnology/Biosafety Unit, CSIR-Crops Research Institute, Kumasi, Ghana.
\textsuperscript{2}Department of Chemistry, Kwame Nkrumah University of Science and Technology, (KNUST) Kumasi, Ghana.

Authors’ contributions

This work was carried out in collaboration among all the authors. Author CAD undertook the study with sampling, preparation, analysis and wrote the first draft of the manuscript. Author PFR managed the performed the statistical analysis and literature review and author DB designed the study and protocol and supervised the work. All authors read and approved the final manuscript.

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ABSTRACT

Fish is an excellent source of high biological value protein, is low in saturated fat, and contains polyunsaturated fatty acids and some vitamins. Mercury occurs naturally in the environment as a result of human activities. In aquatic environments, inorganic mercury is converted into methylmercury (the most common form of organic mercury) by microorganisms present in sediment through accumulations in the aquatic food chain, including in fish and shellfish. Fish absorb methyl mercury from water as it passes over their gills and as they feed on organisms. The objective of the study is to determine mercury pollution levels in fresh fish in Central Market, Kumasi, Ghana. A total of 42 fished were sampled randomly in separate labelled zip lock bags and stored in cold ice chest at different periods comparing of 27 different species after identification. Individual edible fish dorsal muscle tissue was taken and wet dried and analyzed using Cold Vapor
Atomic Absorption Spectroscopy (CV-AAS) method which is really simple, accurate and rapid. The concentration of mercury in fish samples from the marine sea were determined with a mixture of HNO3, HClO4 and H2SO4 for complete oxidation of the organic tissue. The results showed that there was substantial amount of mercury in the fish samples ranged from 15.29 - 981.99 ng/g or ppb wet weight which is less than the FAO/WHO limits of 0.5 ppm wet weight. The study showed low concentrations of mercury in the fish species which do not appear to contribute any significant mercury exposure to the general population. It suggests that a relatively clean marine environment due to minimal industrial activity in the region that has not yet been significantly impacted by mercury contamination.

Keywords: Mercury; methyl mercury; oxidation; cold vapor atomic absorption spectrometry.

1. INTRODUCTION

Global population stands at just over 7 billion and is rising by 78 million people per year and the need to increase food production to make demand for the people [1]. There are many diverse sources of food, and populations around the world have very different diets and demands. In addition to crop and livestock, fish is a stable diet in many countries [1].

Ghana as a country of about 26 million is putting on measures to feed its people in the country by importing food such as fish to boost what we have in the country's agricultural sector [2]. Ghana produces 51% of its cereal needs, 60% of fish requirements, 50% of meat, and less than 30% of the raw materials needed for agro-based industries [3]. Importation of fish has been on the increase but one cannot guarantee the levels of heavy metals such as mercury in these fishes. Hence the need to check these levels of heavy metal in these imported items for health assurance.

Even though certain types of fish can accumulate higher levels of mercury than others, it is widely recognized that there are considerable nutritional benefits to be derived from the regular consumption of fish. Fish is an excellent source of high biological value protein, is low in saturated fat and contains polyunsaturated fatty acids such as essential omega-3 polyunsaturated [4]. It is also a good source of some vitamins, particularly vitamin D where a 150 g serve of fish will supply around 3 micrograms of vitamin D – about three times the amount of vitamin D in a 10 g serve of margarine. Fish forms a significant component of the Australian diet with approximately 25% of the population consuming fish at least once a week [4].

The benefits of omega-3 fatty acids in the diet are becoming increasingly recognized. Omega-3 fatty acids are believed to play a role in protecting against heart disease by a number of means including discouraging blood cells from clotting and from sticking to artery walls or decreasing triglycerides and low-density lipoproteins (LDL’s) [5,6] and also appear to have anti-arrhythmic effects [7]. They are also believed to reduce the risk of stroke caused by blood clots, and play a role in decreasing inflammation and benefiting people with autoimmune diseases [8]. They are understood to have beneficial effects on brain and retina development in children [5,9,6].

Fish is also an excellent source of iodine providing from 25% to 100% of women's Recommended Daily Intake. Recent research has found that some Australians do not get enough iodine [10, 11]. An adequate iodine intake is important for normal thyroid function and is also essential for critical periods in foetal development and early childhood [12]. These all are positive benefits, and a moderate amount of seafood is a healthy addition to the diet. But nearly all fish contain at least a trace amount of mercury, and the concern over this issue hovers over this advice. The risk of mercury poisoning is real if you eat a lot of fish, especially fish that has a high concentration of mercury [13].

Cold-vapor atomic absorption spectrometry (CV-AAS) is one of the most popular techniques for determining mercury in a wide variety of samples [14-19]. Generally, this technique is applied to determine the total mercury content [20]. Despite the considerable global concern about mercury contamination of commercial and recreational fishery products, there is paucity of information on mercury in fish from markets in Ghana. The study seeks to determine the levels of mercury in marine (fresh) fish sample obtained from Kumasi central market for human consumption and compare the values obtained with standards values.
2. MATERIALS AND METHODS

2.1 Study Area

The central market of Kumasi is in the Ashanti region, Ghana which is in the southern part of the country, Ghana with coordinates 6.6977° N and 1.6222° W. Fresh fish that were found on the market were marine fish stored from cold store for sale.

2.2 Collection and Storage

All samples were collected randomly in the research area and packaged in individual labelled zip lock rubber stored in ice chest for analysis. Because the mercury analytical technique is sensitive, great care in sampling protocol were used. All sampling, storage and manipulation device were mercury-free. Because of the risk of mercury in some laboratory environments, all labware and sample collection tools were stored in a clean mercury-free environment. Typical glassware/plastic ware cleaning protocol include; routine laboratory washing, rinsing with rinsing with clean (mercury-free) water, an acidic rinse and further rinsing with laboratory grade clean (mercury-free) water. The acidic rinse may be 10% nitric acid. Rinse times reported are for 12-24 hours at room temperature while some report at 70°C for 24 hours.

2.3 Sampling and Sample Preparation

About fourteen samples of fresh fish in the wet season and twenty eight taken in the dry season were collected from various locations at random at the central market between October 2010 and March 2011. The samples were sorted by species, gathered in separate sample rubber after rinsing with deionized water for identification and stored in refrigerator at freezing point. A portion edible muscle tissue was removed from the dorsal part of each fish, stored in clean capped glass vials and kept in freezer unit analysis. In all 42 samples covering 27 different species were collected.

The dorsal muscles were taken after the total weight and length. These muscles were cut into small pieces and dried wet on a tissue paper for at least 60 - 70% dry. All other matrices require decomposition, typical by wet oxidation mineralization. The organic and inorganic matrix decomposed (digested) and all mercury present were converted (oxidized) to mercury (II) prior to the cold vapor process. The oxidized mercury then is reduced to elemental metallic mercury vapor by one of the cold vapor techniques.

In this way mercury is ensured to be in the soluble (non-volatile) free form of Hg (II), the use of potassium permanganate is describe in equation I

\[
\text{MnO}_4^- + (\text{Inorganic or organic})-\text{Hg} \rightarrow \text{MnO}_2 + \text{Hg}^{2+} + \text{CO}_2 + (\text{Inorganic salts})
\]

2.4 Digestion Procedure

The fish samples were digested for total mercury determination by an open procedure developed at the National Institute for Minamata Disease (NIMD) in Japan. The accuracy of this method has been verified through inter laboratory comparison exercise.

About 0.5g of homogenized fish sample was weighed into 50ml volumetric digestion flask and a mixture of 1ml H_2O_2, 2ml HNO_3-HClO_3 (1:1) and 5ml H_2SO_4 was added. The mixture was then heated at a temperature between 200°C and 250°C until the solution was clear. The sample solution was then cooled and diluted to 50ml with double distilled water. A blank and standard solution digests using 25, 50 and 100 ug/l standard Hg solution were subjected to the same treatment. The concentrations of the standard solution digests obtained were 25, 50 and 100ng National Institute for Minamata Disease (NIMD).

2.5 Determination of Mercury

Determination of mercury in all the digests was carried out by cold vapor atomic absorption spectrophotometry using and Automatic Mercury Analyzer Model HG-5000 developed at NIMD. The analyzer consists on air circulation pump, a reaction vessel, SnCl_2 dispenser, an acidic gas trap and a four-way stop cock with typon tubes to which is attached a ball valve. The operations of the ball valve and the air circulation pump are controlled by microprocessor.

During the determination, a known volume of the sample solution normally 5ml introduced into the reaction vessel using a micropipette (1-5ml). The reaction vessel is immediately stopped tightly and 0.5ml of 10% (w/v) SnCl_2.2H_2O in 1m HCl was added from a dispenser for the reduction reaction. During this time air was circulated through the four-way stopcock to allow the

83
mercury vapor to come to equilibrium and the acidic gases produced by the reaction also swept into the sodium hydroxide solution. After 30 seconds the four-way stopcock is rotated through 90°C and the mercury vapor is swept into the absorption cell [25]. Response was recorded on the strip chart recorder as a sharp peak height were used for computation.

The results and calculation were done by measuring the height of each peak in mm and use in the formula below

\[
\text{Concentration of T-Hg (ng/g or ppb wet wt.)} = \frac{\text{Std Conc. in ng} \times (\text{Peak ht. of sample} - \text{Peak ht. of Blank})}{\text{Peak ht. of Std.} - \text{Peak ht. of Blank}} / \text{Sample weight in gram}
\]

Fish samples were tested for mercury with a cold vapor atomic absorption spectrometer. The samples were then analyzed by the spectrometer and the mercury concentrations were displayed in ng/g or ppb wet weight.

3. RESULTS

A total of 42 marine fish samples comparing of 27 different species were collected at different dates at the same site for six months at the central market in Kumasi. Details are shown in Fig. 1, showing sample name, scientific name, local name, total weight and average concentration. Calculations were done as showed below:

Please check this equation

\[
\text{Std Conc. in ng} \times (\text{Peak ht. of sample} - \text{Peak ht. of Blank}) / (\text{Peak ht. of Std.} - \text{Peak ht. of Blank}) / \text{Sample weight in gram}
\]

Where,

\[
\text{Std concentration in ng} = 50 \text{ ng} \\
\text{Peak height of Std} = 50 \text{ mm} \\
\text{Peak height of blank} = 2 \text{ mm} \\
\text{Peak height of sample} = 28 \text{ mm} \\
\text{Sample weight in grams} = 0.525g
\]

\[
= 50 \text{ ng} \times (28 \text{ mm} - 2 \text{ mm} / 50 \text{ mm} - 2 \text{ mm}) / 0.525g
\]

4. DISCUSSION

Total mercury concentrations in the muscle tissue of different fish species were determined using a rapid, sensitive and accurate procedure as stated above. Mercury content in fish is considered to be good indicator of human exposure to inorganic or methylmercury contamination. That mercury in fish appears to be predominantly in the form of methylmercury. Therefore, diet consisting particularly of fish, could be the main source of exposure to methylmercury in the general population.

![Fig. 1. Scientific name of different species with the corresponding weights and average Total concentration in ng/g](image-url)
Results of total mercury in fish in μg g⁻¹ on wet weight basis from fishes imported into the country, Ghana and neighboring countries are presented in Fig. 1. Mercury levels were determined a total of 42 samples, covering 27 marine fish species. Mercury concentration ranged from 15.29 to 981.99 ng/g or ppb wet weight. The results indicate that the mercury content in the samples studied depends on the fish species and the concentrations showed from the overall results, it can be deducing that concentration were below and above the 0.5 μg/g wet weight limit recommended by the FAO/WHO, 1972 which has been adopted by many countries. Reports indicated that mercury levels in most species of oceanic fish fall in the fall in the range of 0.00 - 0.5 μg/g wet weight with most values close to 0.15 μg/g wet weight [21]. Fish such as swordfish, tuna fish and halibut, whose values usually range from 0.2 – 1.5 μg/g are the few exceptions to this rule of standard values [22]. For example, mercury on the edible portion of various fish species landed at Irish port during 1993 are in the range of 0.1 – 0.39 with mean of 0.1 within which our value fall. These levels are reported to be low and are well within the maximum limits set by the EC for mercury in fisheries product [23]. Mercury concentrations reported here are lower by the order of magnitude when compared to value reported for other topical, less industrialized area like Indonesia, Thailand and Paupua New Guinea (CIFA). This confirms the assertion that geographical location in addition to other factors like metabolic differences appears to be important with regards to the mercury content of fish; and this is further illustrated by the analysis of fish from different location [21].

The FDA reported in 1991 that mercury level in most American fish ranges from 0.1 – 0.5 ppm. Cod fish samples obtained from the strait between Denmark and Sweden, which is heavily contaminated had values up to 1.26μg/g wet weight, cod caught in the area of Greenland had values of 0.012 – 0.036 μg/g wet weight whereas North Sea cod had values in the range of 0.150 – 0.195 μg/g wet weight. In a study of swordfish from six areas extending from Caribbean Sea to the Grand Banks, significant variations from one area to another were observed in average mercury levels [24]. The study showed low concentrations of mercury in the fish species ranging from 15.29 to 981.99 ng/g or ppb wet weight, which do not appear to contribute any significant mercury exposure to the general population. These fishes were imported into the country from Africa countries such as Morocco, Mauritanian, and Senegal etc. It suggests that a relatively clean marine environment due to minimal industrial activity in the region that has not yet been significantly impacted by mercury contamination. These means the importation has to be monitored because of the industrial activity going on in those countries; because one cannot guarantee the levels of total mercury in these fishes.

5. CONCLUSION

In conclusion, this study shows that the mean total concentrations of mercury in edible fish from the central market, Kumasi, Ghana increase in size of the fish with very few exceptions though levels were not significant. All the sample analyzed fell below the WHO/FAO recommended limit. This can be attributed to minimal industrial activity at the coast where these fished came from or reduced mercury concentrations as a result of dilution of high concentrations by the sea water making it relatively clean marine environment that had no significant impact on the fishes but still, there is the need to check the importation of fishes in the country. This study will help researchers to focus on other sources of fishes into our markets such as country coasts, lakes, dams and rivers in Ghana which has not been explored because most fishes found on the market change their form (smoking, drying, salting etc) before they get into the market.

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COMPETING INTERESTS

Authors have declared that no competing interests exist.

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