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Mercury Concentrations in Fish Species from the Gulf of Guinea, Ghana

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Human activities are artificially increasing mercury loads in the atmosphere on a local, regional and even global scale, leading to the contamination of the environment. A relative increase of 1.2% to 1.5% per year of mercury concentrations in the atmosphere over the Atlantic Ocean has been reported suggesting an increasing of direct mercury load to this ocean (Slemr and Langer 1992). Thompson et al. (1992) suggested a similar increase in oceanic deposition of Hg based on the analysis of seabird feathers. This increase in the anthropogenic mercury load to the oceans may reflect in the metal's concentration in fish (Rolfhus and Fitzgerald 1995). Another source of mercury contamination of the oceans is through the discharge of industrial effluents into them. Fish bioaccumulate this toxic metal with potential adverse effects on humans (WHO, 1976; Moffett 1993). With the exception of occupational exposure, fish in the diet has been shown to be the dominant means for human mercury accumulation (United States Environmental Protection Agency 1997). This has been a matter of concern since the toxicity of mercury especially in its organic form as methylmercury was clearly documented (Uchida et al. 1961). Mercury and its organic compounds, especially methylmercury, are known to be capable of damaging the central nervous system (WHO 1976). Methylmercury is an ecotoxicant that bio-accumulates in marine seafood species. The natural sources and anthropogenic sources of mercury released into the marine environment through bacterial processes becomes the bio-accumulating ecotoxic methylmercury. Methylmercury binds to proteins in living organisms and is passed up the food chain where the methylmercury can reach dangerous levels in certain seafood species. Most mercury (>90%) accumulated in fish is methylmercury. This fact has permitted the use of total mercury concentrations as an indication of the whole fish burden of methylated mercury (Bloom 1992).

Since the tragedy of Minamata Bay in Japan (Kurland et al. 1960) and the identification of the likelihood of mercury toxicity from fish consumption in Peru and some coastal regions of the Mediterranean (Piotrowski and Inskip 1981; Inskip and Piotrowski 1985) most concern has centred on the presence of mercury in fish since seafood is a major source of this element. In some instances fish catches have been banned for human consumption because their total mercury content exceeded the maximum limits recommended by the Food and

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Agriculture/World Health Organisation (FAO/WHO 1972). Many countries have also established maximum permissible mercury concentrations in fish for human consumption in the range of 0.5 to 1.0 μg g^{-1} wet weight which has triggered a process of surveying mercury concentrations in natural fish populations in order to protect fisheries and their market (Lacerda et al. 2000). Consequently extensive surveys have been carried out in a number of countries to evaluate the presence of mercury in the aquatic biota including fish, which can often be considered as indicator of marine pollution. The level of mercury found in a fish is related to the level of mercury in its aquatic environment and its place in the food chain (Monteiro et al. 1996). Apart from that mercury also biomagnifies through the food chain; so large predatory fish species tend to have higher levels than non-predatory fish or species at lower levels in the food chain. Recently, levels of mercury in fish have been widely reported (WHO 1976; Nixon et al. 1994; Rolfhus and Fitzgerald 1995; Monteiro et al. 1996; Nakagawa et al. 1997; Voegborlo et al. 1999; Lacerda et al. 2000; Storelli et al. 2002; Love et al. 2003; Storelli et al. 2003). This paper reports the first results of mercury concentrations in a variety of fish species from the coastal waters of Ghana along the Gulf of Guinea.

MATERIALS AND METHODS

All glassware were soaked in detergent solution overnight; rinsed and soaked in 10% v/v HNO_3 solution overnight. They were rinsed with distilled water followed by 0.5% $KMnO_4$ solution and finally rinsed with distilled water before use.

All reagents were of analytical reagent grade (BDH Chemicals Ltd, Poole, England) unless otherwise stated. Double distilled water was used for the preparation of all solutions. Mercury stock standard solution (1000 mg L^{-1}) was prepared by dissolving 0.0677 g of $HgCl_2$ in the acid mixture HNO_3 - H_2SO_4 - $HClO_3$ (2 + 10 + 2) in a 50 ml digestion flask with heating on hot plate at 200° C ± 5 for 30 min. The solution was then diluted to 50 ml with water. Blank solutions were also prepared alongside and bulked together for use as a diluting solution. The working solutions were freshly prepared by diluting an appropriate aliquot of the stock solution through intermediate solutions using blank solution. $SnCl_2 \cdot 2H_2O$ solution (10% w/v) was prepared by dissolving 10 g of the salt in 100 ml 1M HCl. The solution was aerated with nitrogen gas at 50 ml min^{-1} for 30 min to expel any elemental mercury from it.

The fish species were obtained between November 2003 and February 2004 from commercial catches landed at a local fishing port in James Town, Accra. The samples were sorted by species, wrapped in clean plastic bags and stored on ice in an ice chest and transported directly to the laboratory for identification. The samples were washed with distilled water, dried in tissue paper and weighed. A portion of the edible muscle tissue was removed from the dorsal part of each fish, homogenized and stored in clean-capped glass vials and kept in a freezer until analysis. In total 56 samples, covering 20 different species were collected.

The fish samples were digested for total mercury determination by an open flask procedure developed at the National Institute for Minamata Disease (NIMD) in Japan by Akagi and Nishimura (1991). The accuracy of this method has been verified at NIMD through interlaboratory comparison exercises and by participating in the analyses of reference materials supplied by the International Atomic Energy Agency (IAEA). In the procedure, 0.5 g of homogenized fish sample was weighed into 50 ml volumetric digestion flask and digested with a mixture of 1 ml H_2O, 2 ml HNO_3: $HClO_3$ (1:1) and 5 ml H_2SO_4 at 200° C ± 5 for 30 min. The sample solution, which was clear, was cooled and diluted to 50 ml with double distilled water. A blank and standard solution digests using 25, 50 and 100 µl of 1 µg/ml standard Hg solution were subjected to the same treatment. The concentrations of the standard solution digests obtained were 25, 50 and 100 ng. Recovery of mercury was determined by adding increasing amounts of mercury to samples of fish which were taken through the digestion procedure. The resulting solutions were then analysed for mercury concentrations alongside each analytical run.

Determination of mercury in all the digests was carried out by cold vapour atomic absorption spectrophotometry using the Automatic Mercury Analyzer Model HG 5000 (Sanso Seisakusho Co., Ltd, Japan) equipped with mercury lamp capable of operation at 253.7 nm. The signals were obtained on a Yokogawa Model 3021 strip chart recorder. The analyzer consists of an air circulation pump, a reaction vessel, $SnCl_2$ dispenser, an acidic gas trap and a four- way stopcock with tygon tubes to which is attached a ball valve. The operations of the ball valve and the air circulation pump are controlled by a microprocessor.
During the determination, a known volume of the sample solution normally 5 ml is introduced into the reaction vessel using a micropipette (1-5 ml). The reaction vessel is immediately stoppered tightly and 0.5 ml of 10 % (w/v) $SnCl_2 \cdot 2H_2O$ in 1M HCl is added from a dispenser for the reduction reaction. During this time, air is circulated through the four-way stopcock to allow the mercury vapour 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° and the mercury vapour is swept into the absorption cell and response was recorded on the strip chart recorder as a very sharp peak.

RESULTS AND DISCUSSION

The method described in this paper for the determination of mercury in fish provides a rapid, sensitive and accurate system that can be used for routine analysis of fish. It facilitates the relatively rapid (less than 60 min) wet oxidation of samples (0.5-1 g) Recovery studies were performed by spiking samples with suitable aliquots of 1 µg/ml standard Hg solution. Recoveries were 98-102%. Precision and accuracy of the analyses were determined by repeated analyses of samples.
All the fish species analysed in this study are consumed by humans. Results of total mercury in fish in µg g^{-1} on wet weight basis from the coastal waters of Ghana, which is part of the Atlantic Ocean, are presented in Table 1.

Table 1. Total mercury concentrations (μg g^{-1} wet weight) in commercial fish muscle samples from the Gulf of Guinea Ghana, November 2003-February 2004.

Species Name	Common Name	Sample Size	Fresh Fish Weight in g Range (Mean)	Concentration Range	Mean Concentration
Pseudotolithus typus	Flathead captainfish	3	147.0-211.6 (184.9)	0.116-0.191	0.160
Pseudotoilthus senegalensis	Captainfish	3	176.0-215.8 (195.7)	0.010-0.059	0.031
Hemiramphus brasiliensis	Ballyhoo	3	42.7-64.3 (52.1)	0.016-0.031	0.023
Trachinotus goreensis	Longfin pompano	3	138.0-169.4 (153.2)	0.012-0.049	0.027
Caranx crysos	Blue runner	3	264.1-278.9 (271.8)	0.026-0.041	0.035
Selene dorsalis	Guinean moonfish	5	15.3-190.8 (106.3)	0.014-0.061	0.034
Sardinella aurita	Spanish sardine	3	18.4-22.7 (20.3)	0.007-0.012	0.009
Chloroscombrus chrysurus	Atlantic bumper	3	72.1-98.5 (81.9)	0.094-0.129	0.112
Cynoglossus cadenati	Ghanaian tonguesole	3	92.0-428.1 (283.2)	0.027-0.042	0.033
Caranx hippos	Crevalle jack	3	277.8-329.8 (306.6)	0.050-0.072	0.063
Sphyraena guachancho	Guachanche barracuda	3	34.4-49.3 (40.7)	0.009-0.015	0.013
Decapterus punctatus	Round scad	2	24.3-34.8 (29.5)	0.008-0.010	0.009
Dentex canariensis	Canary porgy	2	216.0-234.5 (225.3)	0.075-0.122	0.099
Trachurus trecae	Smallscale scad	2	128.0-131.1 (129.6)	0.087-0.097	0.092
Scomber japonicus	Chub mackerel	2	252.9-277.4 (265.1)	0.037-0.045	0.041
Pseudupeneus prayensis	West African goatfish	3	74.5-117.6 (98.2)	0.054-0.097	0.081
Pomatomus saltatrix	Bluefish	1	815.8	0.126	0.126
-Auxis thazard thazard	Frigate tuna	1	1310.2	0.117	0.117
Galeoides decadactylus	Guinean threadfin	5	66.0-102.62 (81.7)	0.024-0.065	0.041
Trichiurus lepturus	Atlantic cutlassfish	3	75.6-97.4 (82.3)	0.009-0.017	0.013

Mercury levels were determined in a total of fifty-six samples, covering twenty different marine fish species. The results indicate that the mercury content in the samples studied depends on the analysed species. Mercury concentration ranged from 0.007 to 0.191 $\mu g\ g^{-1}$. All the samples had concentration of mercury below the 0.5 $\mu g\ g^{-1}$ wet weight limit recommended by the FAO/WHO (1972) and adopted by many countries (CIFA 1992). The concentrations of mercury in the fish samples are not high when compared to most areas of the world. The concentration of mercury in fish has been the subject of intense study in recent years and the mercury content of marine fish has variously been reported. The first measurements reported in 1934 and in 1940 are in agreement indicating levels from 0.044 to 0.150 $\mu g\ g^{-1}$ wet weight (WHO 1976). Later reports indicated that mercury levels in most species of oceanic fish fall in the range of 0-0.5 $\mu g\ g^{-1}$ wet weight with most values close to 0.15 $\mu g\ g^{-1}$ wet weight (WHO 1976). The most important exceptions to this rule are swordfish, tuna fish, and halibut, whose values usually range from 0.2 to 1.5 $\mu g\ g^{-1}$ (FAO/WHO 1972). Levels in skipjack, white tuna and yellowfin tuna caught in the Atlantic, Pacific and Indian Oceans ranged from 0 to 1.0 $\mu g\ g^{-1}$ wet weight with most values ranging from 0.2 to 0.3 $\mu g\ g^{-1}$ wet weight (WHO 1976). The results of this study are either in agreement or lower than the levels reported by the other authors for marine fish in other areas of the world.

Mercury content in fish is considered to be a good indicator of environmental and human exposure to organic or methylmercury contamination. The main source of mercury to the marine environment is from wet and dry deposition from the atmosphere of inorganic mercury, from natural and anthropogenic, primarily combustion sources (WHO 1976). Rivers that receive industrial effluents also contribute large amounts of mercury to the marine environment. Most of the mercury entering the marine environment then complexes with dissolved or particulate organic matter and may settle with it and accumulate in sediments. If the sediments or bottom water are hypoxic/anoxic, some of the inorganic mercury may be methylated by sulphate-reducing bacteria. Microbially-mediated mercury methylation also occurs in the oxygen-minimum layer of the ocean; this may be the source of methylmercury in the muscle tissues of large pelagic fish such as swordfish and tuna. That mercury in fish appears to be predominantly in the form of methylmercury has been confirmed by many publications (WHO 1976; Bloom 1992). Swedish measurements of freshwater fish, summarized by a Swedish Expert Group (1971), indicated that virtually all of the mercury is present in the form of methylmercury compounds. These findings were confirmed for fish from the North American continent and for swordfish and tuna fish (WHO 1976). Exceptions to this rule are Pacific marlin caught off the coast of Hawaii where methylmercury accounts for only a small fraction of the total mercury (WHO 1976). Therefore, diet consisting particularly of fish, could be the main source of exposure to methylmercury in the general population. The results of this study provide a basis for assessment of human exposure of the coastal population to methylmercury. The generally low levels of mercury found in fish muscle from the coastal waters of Ghana in this study (range 0.007-0.191 $\mu g\ g^{-1}$) suggest that there is very little input or production of methylmercury in the marine

environment. Since fish accumulate more methylmercury than inorganic mercury, the low total mercury levels in fish from this marine environment seems to indicate low concentrations of methylmercury in the Gulf of Guinea. This situation might be attributable to unfavourable conditions for the methylation of mercury along the gulf. Some of the factors controlling the methylation process include mercury concentrations in the sediments, organic matter in the sediments and water column, sulphur in the sediments and pH (WHO, 76). In the presence of elemental sulphur that may be abundant in anoxic sediments, some of the methylmercury may be methylated to form volatile dimethylmercury, which then diffuses into the water column and evaporates into the atmosphere. Under slightly more oxidizing conditions than those required for methylation, methylmercury is demethylated by marine bacteria. Under more strongly reducing conditions in marine sediments, most of the inorganic mercury precipitates as highly insoluble mercuric sulfide (WHO, 1976). The concentrations of mercury in the fish samples obtained in this study are not high when compared to some other areas of the world and can be said to reflect background mercury concentrations that are even much lower than most published mercury concentrations in fish from non-polluted areas of the world. For example mercury in the edible portion of various fish species landed at Irish ports during 1993 are in the range of 0.1-0.39 with a mean of 0.1 within which our values fall. These levels are reported to be low and are well within the maximum limits set by the European Commission for mercury in fisheries products (Nixon et al. 1994). Mercury concentrations reported here are lower by an order of magnitude when compared to values reported for other tropical, less industrialized areas like Indonesia, Thailand and Papua New Guinea (CIFA 1992). This corroborates 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 illustrated by the analysis of fish from different locations (WHO 1976). Cod fish samples obtained from the strait between Denmark and Sweden, which is mercury contaminated, had values up to 1.29 $\mu g\ g^{-1}$ wet weight; cod caught in the area of Greenland had values of 0.012 to 0.036 $\mu g\ g^{-1}$ wet weight whereas North Sea cod had values in the range of 0.150 to 0.195 $\mu g\ g^{-1}$ 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 (WHO 1976). With regards to metabolic differences variations in mercury content in different species of benthopelagic fish were observed despite the fact that they had identical feeding habits and ecological requirements and were exposed to mercury in the same area for the same length of time (WHO 1976).

It can be suggested from the results of this study that all the samples obtained from the Ghanaian coastal waters between November 2003 and February 2004 and analysed for mercury had concentrations below the WHO/FAO recommended limit. The low levels of mercury in the fish species obtained in this study suggest a relatively clean marine environment that has not been significantly impacted by mercury contamination probably due to minimal industrial activity in the region. The result also suggests that the mercury content of the fishes is unlikely to constitute a significant health hazard.

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