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Head Hair Total Mercury and Methylmercury Levels in Some Ghanaian Individuals for the Estimation of Their Exposure to Mercury: Preliminary Studies

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Abstract The extent of human exposure to mercury in some individuals in Ghana was evaluated by analysing samples of human head hair for total mercury and methylmercury. The average level of total mercury was 0.843 μg g^{-1} (in range of 0.119–4.140, n = 123) and that of methylmercury was 0.787 μg g^{-1} (in range of 0.208–1.847, n = 42). Mercury was present in the hair samples almost completely in the methylated form. The average percentage ratio of methylmercury to total mercury was 97.2% (in range of 88.5%–107.6%). The results of this study indicate low levels of exposure to methylmercury and does not pose a significant risk to the individuals and to a greater extent the general population.

Keywords Total mercury · Methylmercury · Head hair · Ghana

Mercury occurs naturally as a mineral and is distributed throughout the environment by both natural processes and anthropogenic activities. Major anthropogenic sources of mercury releases to the environment include mining and smelting; industrial processes involving the use of mercury, including chlor-alkali production facilities; combustion of fossil fuels, primarily coal; production of cement; and medical and municipal waste incinerators and industrial/commercial boilers (USEPA 1997). Mercury emissions are, however, distributed over long distances in the atmosphere and oceans. This means that even countries with minimal mercury emissions, and other areas situated remotely from dense human activity, may be adversely affected. For example, high mercury exposures have been observed in the Arctic, far distances from any significant sources of releases. Once deposited in an aquatic environment inorganic mercury is converted into methylmercury (MeHg) by saprophytic microorganisms and is then bioaccumulated in fish and shellfish through the marine food web (ATSDR 1992). Dietary intake is therefore the most important source of non occupational exposure to mercury by the general population, with fish and other seafood products being the dominant source of mercury in the diet. Most of the mercury consumed in fish or other seafood is the highly absorbable methylmercury. Mercury has been detected in blood, urine, human milk, and hair in individuals in the general population. Even though mercury has been detected in a variety of human tissues, scalp hair has been used in many studies as an excellent bioindicator to estimate methylmercury exposure for human populations (WHO 1990; NRC 2000; Yasutake et al. 2003, 2004) because methylmercury is incorporated into the forming hair and it reflects the methylmercury concentration in the blood at the time the hair was formed. At the time of hair formation, mercury from the blood capillaries penetrates into the hair follicles. As hair growth is approximately 1 cm each month, mercury exposure over time is accumulated in hair strands (WHO 1990) the mercury levels in hair closest to the scalp reflect the most recent exposure, while those

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farthest from the scalp are representative of previous blood concentrations. Evaluation of past exposure is therefore possible since the concentration profile along the hair strand represents a recapitulation of previous blood concentrations i.e. previous MeHg exposure (WHO 1990). However, mercury concentration in the hair can be increased by the adhesion of external mercury vapor and inorganic mercury though they can be reduced or eliminated by hair treatments such as permanent waves, and influenced by the sample collection site. It is generally recognized that the general population is primarily exposed to methylmercury through consumption of fish, and that analysis of head hair is the most appropriate method for monitoring the intake of methylmercury in persons at risk (Abe et al. 1995; Frery et al. 2001). In cases of no exposure to external inorganic mercury or mercury vapor, almost all mercury in the hair is in the form of methylmercury. In such a situation, methylmercury exposure can therefore be evaluated by measuring total mercury (THg). However, since people involved in gold mining and gold refining have a high possibility of contamination from metallic mercury and mercury vapour, evaluation of actual methylmercury exposure is possible only by measuring methylmercury as well as total mercury in the hair. The purpose of this study is to estimate exposure to total mercury and methylmercury in some Ghanaian individuals using hair as a biomarker for mercury contamination of the human body; and to determine the percentage ratio of methylmercury to total mercury in hair as a means of determining the source of exposure.

Materials and Methods

Hair samples were collected from donors by single cutting with a pair of clean stainless steel scissors in accordance with the IAEA protocols. From each subject, a hair sample of approximately 2 cm was taken near the root just above the neck. During the collection of the hair samples, each individual was asked to complete a questionnaire detailing sex, age, dietary habits, socio-demographic variables such as occupation, education, residence history, smoking habits, alcohol drinking, medical and work history. The questions also included fish consumption with an emphasis on fish species consumed and the frequency. A total of 123 hair samples were obtained comprising of 103 males and 20 females. The hair samples were stored in sealed polyethylene bags and shipped to Japan for analysis at the National Institute for Minamata Disease (NIMD). The hair samples were washed with neutral detergent (1:100) in 20 mL glass vials and rinsed well with distilled water. They were washed with acetone and dried under reduced pressure. The samples were then cut into fine pieces in the vial using a pair of dissection scissors. They were stored in a dessicator until analysis.

Methylmercury (MeHg) was determined in 42 out of the 123 samples by the hydrochloric acid elution-toluene extraction and gas chromatography with electron capture detection. In the procedure, 10 mg of each sample was weighed into a 10 mL test tube with a screw cap and 2 drops of ethanol was added. The sample was then covered with some amount of defatted cotton wool to prevent the hair from floating. Three milliliters of 2 M HCl was then added. The test tube with its contents was heated in a water bath at 100°C for 5 min. It was cooled and vortex mixed, followed by centrifugation at 1,200 rpm for 3 min. Using a 1 mL pipette with some defatted cotton wool wrapped around the tip, 1 mL of the extract was carefully taken into a 10 mL conical centrifuge tube with a glass stopper and 2 mL toluene added. It was shaken for 3 min and centrifuged at 1,200 rpm for 3 min. The aqueous layer was discarded and the toluene layer obtained for gas chromatographic analysis. The toluene extract was injected into Yanaco Gas Chromatograph Model G3800 with column temperature of 150°C; injector and detector temperature of 200°C. Column was 3.0 mm × 1.0 m glass packed with Hg-20A on Uniport HP AW-DMCS, 60–80 mesh (GL Science Co. Ltd., Tokyo, Japan) and carrier gas was nitrogen. For total mercury (THg), 123 samples were digested by an open flask procedure developed at NIMD (Akagi and Nishimura 1991; Voegborlo and Akagi 2007). This involved the digestion of about 0.1 g of the sample using 1 mL water, 2 mL mixture of nitric acid, perchloric acid (1 + 1) and 5 mL sulphuric acid added in turns; and heated at a temperature of 200°C in a 50 mL digestion volumetric flask. The digests were diluted to volume with double distilled water and analysed by cold vapour atomic absorption spectrophotometry using an automatic mercury analyzer HG-201 (Sano Seisakusho Co. Ltd, Tokyo, Japan). The data obtained in the study were subjected statistical treatment using descriptive and analytical statistics in SPSS Statistical Package Version 10.1.

Results and Discussion

A total of 123 head hair samples were analyzed for total mercury and 42 out of the 123 samples for methylmercury levels. Precision and accuracy of the analytical methods used were evaluated by repeated analysis of some samples and Human Hair Certified Reference Material NIES CRM No. 13 (National Institute for Environmental Studies, Japan). The validity of the methods has been proven by agreement between values obtained for the measured (3.67 ± 0.05, $n = 4$ for THg and 3.60 ± 0.09, $n = 4$ for MeHg) and the certified (4.42 ± 0.2 μg g^{-1} for THg and

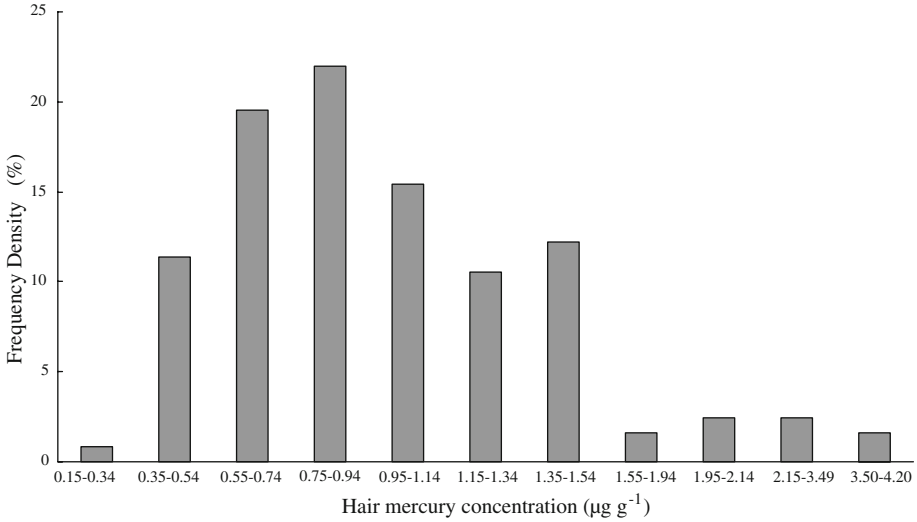

Fig. 1 Distribution of total mercury concentrations in hair of some individuals in Ghana

3.8 ± 0.40 for MeHg). Detection limit of the method was 0.5 ng g^{-1} for THg. The distribution of total Hg concentration in the 123 hair samples is presented in Fig. 1.

The average level of total mercury (mean ± SD) in the hair samples was 0.843 μg g^{-1} ± 0.557 (in range of 0.119–4.140, median: 0.728, n = 123) which were all below the World Health Organisation (WHO) safety limit of 10 μg g^{-1} above which adverse effects on brain development are likely to occur (WHO 1990). These levels are lower than levels (0.89–6.50) reported for 53 people majority of whom were gold miners and a few living in riverine villages, having little or no direct contact with gold mining activities in the Pra River Basin in Ghana (Donkor et al. 2006) and far lower than values reported for Brazil (8.89 μg g^{-1}, Madeira River and 16.2 μg g^{-1}, Tapajos River) and the Philippines, 4.14 μg g^{-1} where artisanal mining operations are also prevalent. Adimado and Baah (2002) also reported hair total mercury levels for some artisanal gold miners in the Ankobra (0.15–5.86, mean = 2.65, n = 100) and Tano (0.06–28.3, mean = 3.45, n = 117) River Basins in Southwestern Ghana which were generally higher than values obtained in this study. Different factors have been reported to influence hair mercury concentrations (Frery et al. 2001; Dolbec et al. 2001). In this study factors such as age, sex, educational level, place of residence, alcohol consumption, smoking, fish eating habits and use of mercury containing cosmetic products and medicines were considered in an interview-administered questionnaire. None of the factors were found to influence mercury concentration in the hair of the individuals according the statistical analysis using SPSS Statistical Package. This could be attributed to the scattered nature of the sample population being individuals with varied background, who are mainly resident in ten different major cities in Ghana. Mercury in hair is a good indicator of Hg blood levels, particularly when an individual is exposed to organic mercury of dietary origin. In humans, monomethyl mercury (MMHg) is distributed between blood and hair in a ratio of 1:250 (WHO 1990). A daily average methylmercury intake of 0.1 mg/kg body weight per day by an adult woman is estimated to result in hair mercury concentrations of about 1 mg g^{-1}, cord blood levels of about 5–6 mg/L and blood mercury concentrations of about 4–5 mg/L though, there are limitations, uncertainties and variability in these estimates (NRC 2000) Significant Hg levels have been reported for populations living in artisanal gold mining areas contaminated with mercury. For example, a high level of total mercury, 151.2 ppm, was found in hair from people who lived in Brasilia Legal, which is located about 100 km downstream from Itaituba, the main gold-trading center in the Tapajos River basin (Akagi and Naganuma 2000). Malm et al. (1990) also reported levels of total mercury in human hair from Madeira river area (0.22–40.0, mean 9.2 μg g^{-1}). In their studies, the total mercury levels in hair of people from Mato Grosso gold mining area, who did not consume any fish diet ranged from 0.04 to 6.3 μg g^{-1} with an average value of 2.4 μg g^{-1} whereas people in Tapajos goldmining area, who consumed fish diet had higher hair mercury concentrations ranging from 10.0 to 31.8 μg g^{-1} with an average of 18.7 μg g^{-1}. They also confirmed using a control group in Rio de Janeiro that people with a common fish diet had 5.4 μg g^{-1} on average with a range from 1.5 to 13 μg g^{-1}, whereas people with no regular fish diet had only 1.7 μg g^{-1} on the average, with a range from 0.9 to 3.1 μg g^{-1}. Therefore, the low concentrations of hair mercury in this study comparable to levels obtained for the people with no regular fish diet could be considered to be the result of low exposure to methylmercury through the consumption of fish. It should be interesting however, to note that the highest level of total mercury (4.14 μg g^{-1}) obtained in this study was from an individual who was

resident in the coastal town of Cape Coast for twenty-two (22) years and ate large amounts of fish daily according to the questionnaire. Significant Hg levels have also been reported for populations living in regions not exposed to human polluting activities, but who eat large amounts of fish. Values ranging from 10.2 to 35.9 μg g^{-1} were obtained for people living in fishing villages (Akagi and Naganuma 2000). In Papua New Guinea, an average hair Hg level of 4.2 μg g^{-1} was reported for villagers on the coast, whereas an average of 1 μg g^{-1} was obtained in the hair of inhabitants living 25 km inland (Suzuki 1991). Similarly at the village of Ponta de Pedras, which is far downstream on the Tapajos River in Brazil, relatively low levels of mercury in hair were reported (Akagi and Naganuma 2000). In another study among native Amerindian communities in French Guiana, differences were observed between the study sites. In people living in Cayode, located on the Tampok River, Hg concentrations were slightly higher than in the people living farther upstream along the Maroni River (12 ± 3.5 μg g^{-1} at Cayode, 11.1 ± 4.2 μg g^{-1} at Twenke/Taluhen, and 11.2 μg g^{-1} at Antecume Pata). The average Hg concentrations for Cayode remain statistically higher than the others (Frery et al. 2001). High concentration of mercury (Hg) in hair has been reported for Cambodians resident in Phnom Penh (Agusa et al. 2007). To confirm the Hg contamination occurring through intake, Hg concentrations were determined in both hair and blood of the residents of Phnom Penh (n = 20). Mercury concentrations in the hair and blood were 0.69–190 μg g^{-1} dry wt and 5.2–58 μg L^{-1}, respectively, which were lower than those from Hg contaminated or high fish intake regions, but were higher than those from non-contaminated regions. Some female subjects had hair and blood Hg levels exceeding the threshold values for neurotoxic effects (Agusa et al. 2007). Olivero-Verbel et al. (2008) reported hair THg in inhabitants of different fishing areas along the Caribbean coastal shoreline of Columbia to vary between 0.1 and 21.8 μg g^{-1} with an average of 1.52 μg g^{-1} and a median of 1.1 μg g^{-1} to which our results are quite close. In general, several studies have shown that Hg levels in hair are higher for residents of areas contaminated by mercury than for residents of uncontaminated regions. In this study, the samples analysed were mostly from individuals who were resident inland away from artisanal gold mining areas and also away from the coast. The results are therefore comparable to levels obtained for inhabitants living inland elsewhere and can be considered background. MeHg and THg concentrations were determined in 42 samples simultaneously to determine the ratio (MeHg/THg). Mercury was present in the hair samples almost completely in the methylated form as the average percentage ratio of methylmercury to total mercury was 97.2% (in range of 88.5–107.6). Figure 2 presents the comparison indicating no significant difference between the means of THg and MeHg.

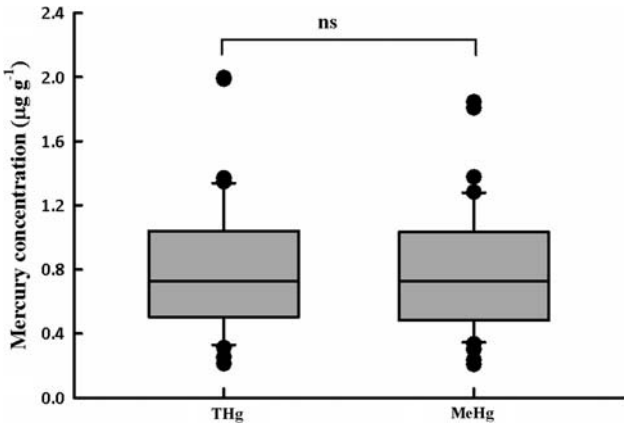

Fig. 2 Comparison between THg and MeHg in the hair of some individuals in Ghana. The lower and upper margins of the box represent the 25th and 75th percentiles, with the extended arms representing the 10th and 90th percentiles, respectively. The median is shown as the horizontal line within the box. Outlying points are shown individually. ns indicates no significant difference at $p = 0.05$ (Student's t test)

Similar observations were reported by other authors (Akagi et al. 1995; Lebel et al. 1996; Akagi and Naganuma 2000) where levels of methylmercury in human hair were very close to the levels of total mercury in almost all samples collected from the inhabitants of fishing villages in the Tapajos River Basin. This is indicative that the villagers were exposed mainly to methylmercury through fish consumption. Exposure to inorganic mercury as the predominant form in the hair of miners was confirmed in the study of Donkor et al. (2006) where the proportion of MeHg to THg in head hair of individuals were below 50% of the THg with the exception of few individuals among the riverine population downstream. Most epidemiologic studies commonly use mercury levels in hair as the only indicator to estimate human exposure to methylmercury through fish consumption (Canuel et al. 2006). According to data reported on dose–effect relationships in humans, MeHg level of 50–125 μg g^{-1} in hair is considered the minimum level at which clinical symptoms may occur (WHO 1990). Thus adults with 50 μg g^{-1} mercury in hair, corresponding to a daily intake of 0.2 mg Hg, would have a low risk of neurological damage. However, the fetus is more sensitive, and psychomotor retardation has become detectable with maternal hair concentration as low as 20 μg g^{-1} during pregnancy (WHO 1990).

According to the results of this study, the hair Hg concentrations obtained for the individuals can be considered background and are not high enough to cause health effects since the results fall within the range (0.4–6.0 μg g^{-1}) reported by WHO (1990) to be for a normal person. A concentration of 50 μg g^{-1} is considered to be neurotoxic.

The results of this study therefore indicate low levels of exposure to methylmercury through fish consumption which does not pose a significant risk to the individuals and to a greater extent the general population. However fish dietary intake studies in Ghana are needed particularly among populations in the coastal and artisanal gold mining areas in order to be able to relate the actual fish consumption patterns among populations to hair mercury levels, since the main source of methylmercury intake by humans is through fish diet.

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