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Environmental and Occupational Exposures to Mercury Among Indigenous People in Dunkwa-On-Offin, a Small Scale Gold Mining Area in The South-West of Ghana

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Abstract Total mercury concentrations in human hair and urine samples were determined to ascertain the extent of environmental and occupational mercury exposure in Dunkwa-On-Offin, a small scale gold mining area of the central-west region of Ghana. In all ninety-four (94) hair and urine samples comprising of forty (40) small scale miners and fifty-four (54) farmers were collected and analyzed for their total mercury levels using the cold vapour atomic absorption spectrometry. The hair total mercury concentrations ranged from 0.63 to 7.19 ug/g with a mean of 2.35 ± 1.58 ug/g for the farmers and 0.57–6.07 ug/g with a mean of 2.14 ± 1.53 ug/g for the small scale gold miners. There was no significant correlation between the total mercury concentration and the average weekly fish diet. The total mercury concentrations in urine of the miners were higher than those of the farmers and ranged from 0.32 to 3.62 ug/L with a mean of 1.23 ± 0.86 ug/L. The urine concentrations of farmers ranged from 0.075 to 2.31 ug/L with a mean of 0.69 ± 0.39 ug/L. Although the results indicate elevated internal dose of mercury the current levels of exposures do not appear to pose a significant health threat to the people.

Keywords Total-mercury · Hair · Urine · Farmers · Small scale miners · Dunkwa On-Offin

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Artisanal and small-scale gold mining (ASGM) remains the largest global use sector of mercury. It reportedly continues to increase with the upward trend in the price of gold and is the largest source of environmental release from intentional use of mercury. ASGM is inextricably linked with issues of poverty and human health. According to the UNIDO/UNDP/GEF Global Mercury Project (Telmer and Veiga 2008), at least 100 million people in over 55 countries depend on ASGM – directly or indirectly – for their livelihood, mainly in Africa, Asia and South America. ASGM is responsible for an estimated 20–30% of the world's gold production.

In Ghana (formerly called Gold Coast), the government legalized the use of mercury for Artisanal Small Scale Gold Mining in 1989 thereby increasing the toxin into the environment (Donkor et al. 2006a). Between 1994 and 1999, approximately 25,100 kg of mercury were imported to Ghana from Europe and North America and about 97% of it was destined for the Artisanal Small Scale Mining sector (Amegbey and Eshun 2003). The Offin River is known for alluvial gold production and artisans usually recover about 30% of the available gold through primitive hand methods. Gold have been produced from the Offin river valley more than from any other river system in Ghana (Griffis et al. 2002) and as in many other regions of the world, elemental mercury is used in liquid form for amalgamation of gold particles in placer deposits. The gold miners are directly exposed to inorganic mercury and residents of downstream communities are exposed to methylmercury via consumption of fish. The purpose of this study is to evaluate the extent of mercury exposure of small scale gold miners using human hair and urine as the biomarkers. This cross sectional study involved 40 miners (exposed population) and 54 farmers (un-exposed population).

Materials and Methods

The study area (Fig. 1) is part of the Upper Denkyira District (with a population of 108,482 and a land area of 1,139 km^2) of the Central Region of Ghana with Dunkwa-o-Offin as the district capital. The district is defined by latitude 5^{o}N and $5^{o}48'$ and longitude $1^{o}10'$W and $2^{o}30'$W. The Upper Denkyira District is part of an extensive drainage basin known as the Pra basin, comprising the Pra River and its tributaries. The Offin river, a tributary of the Pra drains Dunkwa and it is known for alluvial gold production where artisans usually recover available gold through primitive hand methods. Gold have been produced from the Offin river valley more than from any other river system in Ghana and as in many other regions of the world, elemental mercury is used in liquid form for amalgamation of gold particles in placer deposits.

The communities in the Dunkwa On-Offin area where small scale mining activities take place were visited. Majority of the population were farmers with the youth indulging in small scale mining. At each community, those who volunteered had their hair cut in such a way that it did not alter their normal hair-do in accordance with the IAEA protocols. The hair samples were put into separate envelopes with the age, sex, weight, dietary habit, rate and fish species consumed, occupation and residence history of the individuals from whom the samples are collected indicated through an administration of a questionnaire. Spot urine samples (n = 90) of the individuals were also collected into 100 mL sterile plastic containers, sealed and stored on ice. The informed consent was obtained from all the donors before they could participate in the study. The study cohorts consisted of 54 farmers (41 males and 10 females) and 40 miners (30 males and 10 females). The age of the farmers ranged from 18 to 65 and the miners ranged from 19 to 53. The samples were transported to the laboratory at the Department of Chemistry, Kwame Nkrumah University of Science and Technology, Kumasi, Ghana for analysis.

In the laboratory the hair samples were washed first with acetone and then with deionized water and dried in the oven at 50°C to constant weight. The hair samples were digested for total mercury determination by an open flask method. The accuracy of this method has been verified by participation in the analysis of certified reference materials supplied by the International Atomic Energy Agency (IAEA).Weighed quantities of each sample were put into separate boiling tubes in triplicates. To each tube containing 0.5 g of the hair sample was added 1.0 ml of distilled water, 2.0 mL of HNO_3:$HClO_4$ in the ratio of 1:1 and 5.0 mL of H_2SO_4. For the urine samples the same procedure was adapted except that no distilled water was added and 1.0 ml of the sample was used. The contents of the boiling tubes were digested on a sand bath at 250°C until the solutions were clear. The solutions in the tubes were allowed to cool to room temperature and made up to 50 ml mark in a graduated flask with double distilled water.

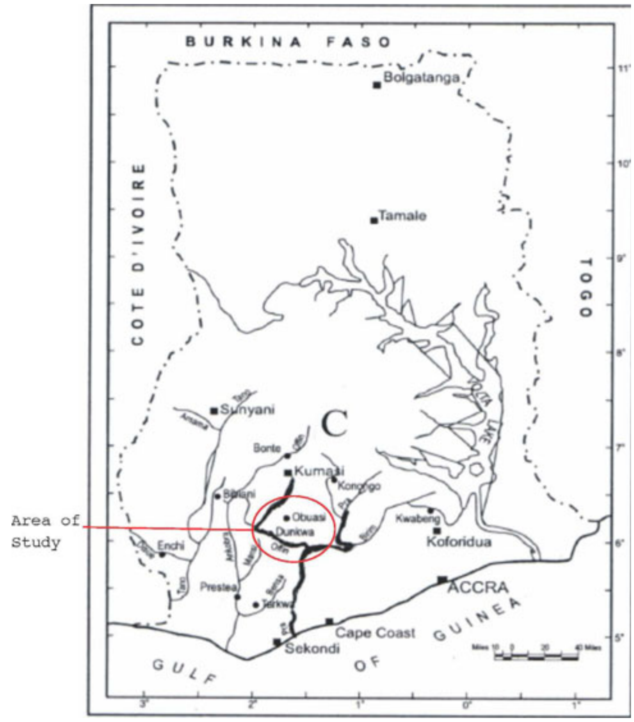

Fig. 1 Map of Ghana showing the study area. The *dark line* represents the Pra river and its main tributary, the offin river

For the urine samples, 20.0 ml aliquots were digested with 20.0 mL HNO_3, $HClO_4$ and H_2SO_4 in the ratio of 1:1:3 and reduced to a final volume of about 20.0 mL by heating at 50°C to minimize the loss of Hg by volatilization. The digest was topped up to the 50 mL mark of a volumetric flask. A blank and standard digest using 25, 50, and 100 uL of 1uL mL^{-1} standard Hg solution were subjected to the same treatment. The treated samples were put in glass bottles and analyzed for their mercury contents by the cold vapour atomic absorption spectrophotometry using an Automatic Mercury Analyzer model HG 5000 (Sanso Seisakusho co., Ltd, Japan) equipped with a mercury lamp at a wavelength of 253.7 nm.

Quality assurance samples analyzed included digestion blanks, replicate samples, pre-digestion spikes and post-digestion spikes. The recovery rate and Method Detection Limits were also carried out. Hair and urine samples were spiked with various concentrations of mercury for recovery repeatability tests and for verifying the analytical methodology. For each run, triplicate samples, spiked samples and blanks were carried through the same digestion procedure. The results are presented in Table 1.

Statistical analysis of data was carried out using SPSS package program and one-way analysis of variance (ANOVA). Differences in mean values were accepted as being statistically significant if $p < 0.05$ or less.

Results and Discussion

The MDL was determined as three times the standard deviation of the digested blank samples. It was found to be 0.05 ug/g for the hair samples and 0.045 ug/L for the urine samples. The percentage recovery of Hg added to urine samples were greater than 90% (data not shown).

In this study, the occupationally exposed people (mine workers) had the highest mean levels of total mercury in both hair and urine. The mean total mercury concentration in the hair of the farmers in the community was 2.35 ± 1.58 with a median of 1.67 and range of 0.63–7.19 (Table 1) and for the small scale miners the mean value was 2.14 ± 1.53 with a median of 1.58 and a range of 0.57–4.23 (Table 2). These are comparable with those reported by Donkor et al. (2006b) in a small scale gold mining area of the Pra River Basin in Ghana but lower than the World Health Organization (WHO) safety limit of 10 ug/g above which adverse health effects may occur (WHO 1990).

Significant mercury levels have been reported in biological samples from populations living in artisanal gold mining areas in Ghana. For example, Adimado and Baah (2002) reported hair total mercury levels for some artisanal gold miners in the Ankobra (0.15–5.86 ug/g, mean = 2.65 ug/g) and Tano (0.06–28.3 ug/g, mean = 3.45 ug/g) River Basins in Southwestern Ghana which were generally higher than values obtained in this study.

In comparison to the results of this study, high total mercury level of 151.2 ug/g, was found in hair from people living in Brasilia Legal, located about 100 km downstream of Itaituba, the main gold-trading center in the Tapajos River basin in Brazil (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 L ug/g). According to their reports, 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 L ug/g with an average value of 2.4 L ug/g whereas people in Tapajos gold mining area, who consumed fish diet had higher hair mercury concentrations ranging from 10.00 to 31.8 L ug/g with an average of 18.71 ug/g. However, in the same study, a control group in Rio de Janeiro with a common fish diet had average total mercury level of 5.4 L ug/g with a range of 1.51 to 13 L ug/g, whereas people with no regular fish diet had only 1.7 L ug g^{-1} average total mercury, with a range of 0.9 to 3.1 L ug/g.

The average weekly number of fish meal for the farmers was 6 and for the small scale miners were 5. The concentration of mercury in hair samples correlated poorly positive with the number of weekly fish meal among the farmers and the miners who ate fish. Although the farmers had high hair average total mercury than the miners, the level is quite low. The low concentration of hair total mercury in this study compared to those with no regular fish diet, it could be said that the people have low exposure to methylmercury through the consumption of fish.

In this study, the mean total mercury concentration in the urine of the farmers in the community not exposed directly to mercury was 0.69 ± 0.39 ug/L with a median of 0.66 ug/L; and a range of 0.08–2.31 (Table 1) and for the small scale miners directly exposed to mercury the average

Table 1 T-Hg levels in hair and urine of farmers (n = 54)

Subjects	Mean T-Hg in hair (ug/g)	Range of T-Hg (ug/g)	Median T-Hg (ug/g)	Mean T-Hg in urine (ug/L)	Range of T-Hg (ug/L)	Median T-Hg (ug/L)
Males	2.48 ± 1.66	0.63–7.19	1.70	0.68 ± 0.41	0.08–2.31	0.61
Females	1.43 ± 0.67	0.71–3.01	1.26	0.59 ± 0.31	0.32–1.22	0.51
Total	2.35 ± 1.58	0.63–7.19	1.67	0.69 ± 0.39	0.075–2.31	0.66

Table 2 T-Hg levels in hair and urine miners (n = 40)

Subjects	Mean T-Hg in hair (ug/g)	Range of T-Hg (ug/g)	Median T-Hg (ug/g)	Mean T-Hg in Urine (ug/L)	Range of T-Hg (ug/L)	Median T-Hg (ug/L)
Males	2.37 ± 1.59	0.61–6.07	1.66	1.39 ± 0.91	0.41–3.62	1.23
Females	1.72 ± 0.89	0.57–4.23	1.17	0.72 ± 0.43	0.32–1.84	0.58
Total	2.14 ± 1.53	0.57–6.07	1.58	1.23 ± 0.86	0.32–3.62	0.86

was 1.23 ± 0.86 ug/L with a median of 0.86 ug/L and a range of 0.32–3.62 (Table 2). The miners were found to have higher levels of total mercury in their urine than the farmers although the concentrations were far lower than the WHO threshold limit. This suggests that the method used in the amalgamation and burning of the amalgam involving an improvised retort is effective in regulating the amount of mercury released into the immediate vicinity. The urinary mercury concentration determined in this study is about 325% lower than that found in mine workers from Rio-Rato, a gold mining community in the Amazons, Brazil (Silbergeld et al. 2004). Recently, it was reported that about 36% of the gold miners working with amalgam in northern Tanzania had urinary mercury concentrations exceeding the WHO guideline value of 50ug L^{-1} (Van Straaten 2000). Wilhelm et al. (2002) found a weak positive correlation between total mercury (T-Hg) concentrations in hair and in urine for children in Germany. However, in this study there was significantly positive, linear correlation between urine T-Hg and hair T-Hg for the farmers ($R^2 = 0.46$). The correlation coefficients for the males and the females were 0.45 and 0.87 respectively, with $p < 0.005$ in each case (Fig. 2). Although the concentrations of T-Hg in hair and in urine of the farmer were low, there was a significant relationship between the two with the extent of relationship being stronger for the females than for the males. This suggests that concentration of mercury in hair is a good predictor of urine mercury levels in the population studied.

The miners also had a significantly positive linear correlation between urine T-Hg and hair T-Hg ($R^2 = 0.66$, $p < 0.005$), but the extent of the association was stronger for the males ($R^2 = 0.58$, $p < 0.005$) than for the females ($R^2 = 0.42$, $p < 0.005$; Fig. 3). This result is similar to that reported by Ohno et al. (2007) who had a positive correlation between mercury levels in hair and in urine ($p < 0.001$). The high correlation between the hair mercury content and urine mercury concentration in this study suggests that analysis of hair can be considered as an alternative method to the analysis of urine though the sampling procedure is much easier than urine sampling. Nonetheless, both methods contribute to a comprehensive determination of T-Hg exposure with hair mercury analysis said to be better for the determination of the body burden related to methyl mercury, whereas the analysis of urine mercury is claimed to be a better indicator for inorganic mercury exposure (Berglund et al. 2005).

According to the results of this study, the hair T-Hg concentrations obtained for the farmers and the miners can be considered background and are not high enough to cause health effects since the results fall within the range (0.4–6.0 ug/g) reported by WHO (1990) to be for a normal

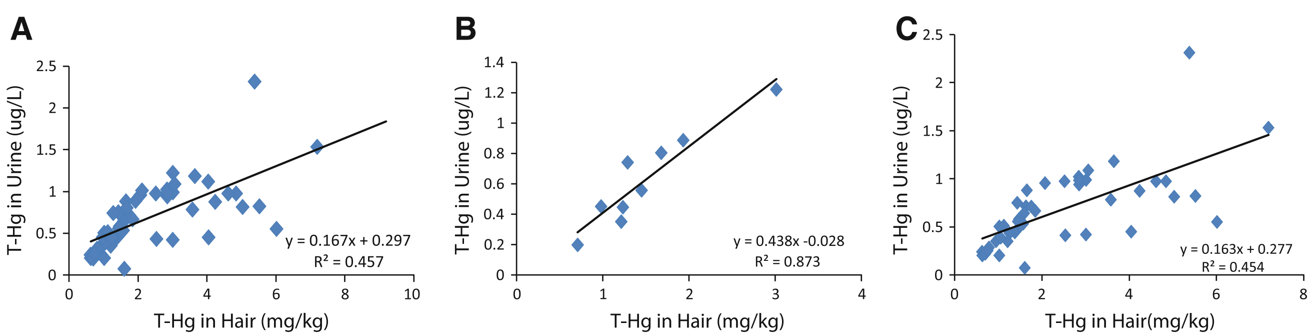

Fig. 2 **a** Plot of T-Hg in urine versus T-Hg in hair of farmers. **b** Plot of T-Hg in urine versus T-Hg in hair of female farmers. **c** Plot of T-Hg in urine versus T-Hg in hair of male farmers

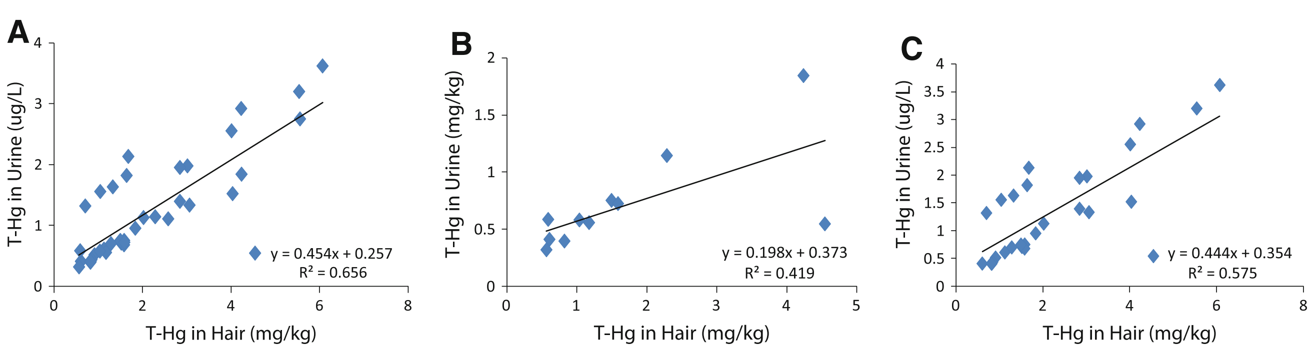

Fig. 3 **a** Plot of T-Hg in urine versus T-Hg in hair of miners. **b** Plot of T-Hg in urine versus T-Hg in hair of female miners. **c** Plot of T-Hg in urine versus T-Hg in hair of male miners

person. The results of this study therefore indicate low levels of exposure to total-mercury through consumption of fish, vegetables, food stuffs and water which do not pose a significant risk to the individuals and to a greater extent the general population in the mining community of Dunkwa-On-Offin. However, fish dietary intake studies in Ghana are needed particularly among the 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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