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Mercury in Human Blood, Urine, Hair, Nail, and Fish from the Ankobra and Tano River Basins in Southwestern Ghana

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Ghana produces over 45 tons of gold per annum, which has now surpassed cocoa as the country's chief foreign exchange earner, bringing over $600million annually (Boroughs 1997). Most of Ghana's existing gold mines are located in the South - Western part of the country, which represents an area of 40,000km^2 that is one-sixth of the country. This auriferous region (Fig.1), is drained by three major rivers which include Pra(18,734km^2, basin), Ankobra(7,148km^2, basin) and Tano(13,694km^2, basin).Over 90% of gold produced in Ghana is from large-scale underground or surface mining. A greater proportion of the remaining 10% is from small-scale mining locally referred to as 'galamsey' (gather and sell) and these operatives are currently estimated at over 100,000. The majority of the small-scale miners extract gold along most of the rivers draining areas underlain by Birimian and Tarkwaian banket reefs. Methods employed by these miners include panning, pitting, sluicing and washing to concentrate the ore. Some of these processes are not carefully controlled and cause adverse effects to the environment including the diversion of rivers and water pollution from the introduction of sediments and mine effluents. Often the small-scale miners use mercury for gold extraction. The concentrated ore is amalgamated and the gold-mercury amalgam is then heated to vaporize and expel the mercury. Some of the miners are therefore directly exposed to these mercury vapours.

Inorganic mercury released into the environment undergoes bio- transformation into methyl mercury species, which bio-accumulate in the tissue of fish and other organisms, and may bio-magnify through the food web. Hence fish and the supporting ecosystem are affected by increasing levels of these substances in the rivers. Humans are exposed to mercury through ingestion of contaminated water and food. Mercury levels in blood may be highly influenced by heavy fish intake. People who do not usually eat fish and have no occupational exposure have mercury levels in whole blood of $\leq$5μg/L (WHO 1980). Moderate consumption of fish containing mercury may give blood levels of 10 - 20μg/L, whilst in heavy consumers, values of 100 - 200μg/L or even more may be observed (WHO 1980). Mercury levels in hair are also to a great extent influenced by fish consumption. Heavy consumption of contaminated fish may show levels of 20 - 50μg/kg hair mercury. The general level of urine mercury in non-exposed subjects is usually below 0.5μg/L, although much higher concentrations have been reported (WHO

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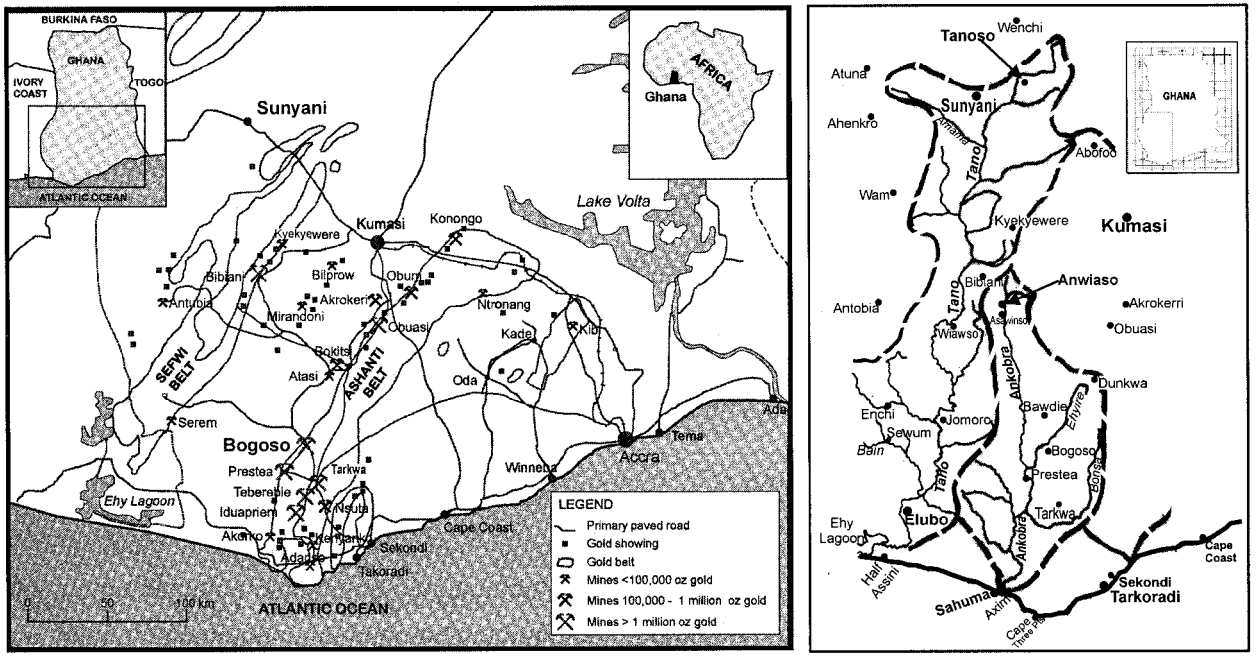

Figure 1 Sampling Locations in the Ankobra and Tano River Basins

1976; Friberg and Vostal 1972). It is likely that some small-scale miners in Ghana have died through mercury intoxication but there are no official records of such casualties. The report presented here is part of a project designed to study the exposure to mercury as a result of gold mining in Ghana. In this study, we have examined total mercury concentrations in blood, urine, hair and nail samples from 217 subjects (12 – 18 years) in the Ankobra and Tano river basins where most of the gold mines are located. These human subjects are of school going age and may be involved in some 'galamsey' activities. In addition, total mercury levels in fish commonly consumed by the public in terms of species and size from four locations in the basins have also been determined.

MATERIALS AND METHODS

The study involved sample collection from four towns: Anwiaso near Asawinso(upstream) and Sahuma near Axim (downstream) in the River Ankobra basin; Tanoso(upstream) and Elubo(downstream) in the River Tano basin (Fig1). In collaboration with the Ghana Ministry of Health, blood, urine, hair and nail samples were taken from a total of 217 subjects at the various locations into preconditioned sample tubes, stored at 4°C and transported to the laboratory. Fish samples were also taken from the two rivers at the corresponding town locations.

Blood samples were centrifuged at 1,500 rpm for 30 min to separate the plasma from the serum. A measured volume of each serum was transferred into a 50 mL volumetric flask. To each flask was added 4 mL concentrated H_2SO_4 + 1 mL concentrated HNO_3 and heated at about 60°C for 2 hr. The samples were then cooled to 4°C in ice bath and to each sample was added 5 mL of 5% $KMnO_4$ and 8 mL 5% $K_2S_2O_8$. The samples were left overnight at room temperature. The excess oxidising agent was reduced by the addition of 1 – 3 drops 10% $HO.NH_3Cl$ and then diluted to 50 mL mark. 1 – 3 drops of 10% n-octanol in ethanol was used as antifoaming agent.

A measured volume of each urine sample was transferred into a 50 mL volumetric flask and to each sample was added about 0.3g $KMnO_4$ mixed thoroughly to dissolve and heated gently under reflux for about 2 hr. Some $KMnO_4$ was added where necessary until excess was permanently present. To each cooled sample was added 1 – 3 drops of 10% $HO.NH_3Cl$ to reduce any excess oxidising agent. Several drops of phenol red indicator are added to each sample followed by concentrated NH_3 until the indicator attains its full red colour. 2 mL dilute H_2SO_4 was added to each sample and allowed to stand overnight prior to analysis.

Hair, Nail and Fish tissue samples were prepared in the same manner. To each weighed sample was added 4 mL concentrated H_2SO_4 + 1 mL concentrated HNO_3 and heated to about 60°C until all organic matter were completely dissolved. The samples were cooled to 4°C in an ice bath and to each sample was added 5 mL of 5% $KMnO_4$ + 8 mL of 5% $K_2S_2O_8$ solution and left overnight at room temperature. 1 – 3 drops of 10% $HO.NH_3Cl$ was added to each sample to reduce

any excess oxidising agent, and quantitatively transferred into a 50 mL volumetric flask and diluted to mark.

Total mercury in the samples was determined by CVAAS. Reagents employed were all of analytical grade and the equipment used is a Perkin-Elmer model 5100PC Atomic Absorption Spectrophotometer equipped with FIMHS (a flow injection mercury hydride system), AS-90 auto sampler and mercury hollow cathode lamp. A standard mercury solution (1.0 mg/mL Hg) was prepared by dissolving 0.1354g $HgCl_2$ in 10% HNO_3 in a 100 mL volumetric flask. 1 mL of this stock solution was transferred into a 1 L volumetric flask and treated with concentrated H_2SO_4, 5% $KMnO_4$, 5% $K_2S_2O_8$ and 10% $HO.NH_3Cl$ and diluted to volume. The concentration of the resulting solution is 1000 μg/L. Calibration standards of concentrations, 5, 10, 25, 50 and 100 μg/L were prepared. Solutions of 3% HCl and 1% $SnCl_2$ + 3% HCl were used as carrier solution and reducing agent respectively (Colin 1994; Larry et al. 1991).

RESULTS AND DISCUSSION

The analyses were carried out under optimised instrumental conditions. The precision and accuracy were assessed via the relative standard deviations of the replicate analyses and recovery tests respectively. The distribution of the relative standard deviations during the analysis of urine samples of the Tanoso subjects are shown in Table 1.

Table 1. Statistics of Relative Standard Deviations of 50 urine samples of Tanoso subjects.

% RSD	Frequency
< 2	11
2 - 4	13
4 – 6	11
6 – 8	10
8 – 10	4
>10	1
	Total = 50

Over 95% of replicate analyses have %RSD < 10% which is an indication of high precision of the within batch measurements of mercury. Recovery tests were also performed on the first 25 urine samples from the Tanoso subjects by standard addition of 2 μg/L Hg solution. The average recovery of 95.1% obtained from a scatter diagram (Fig 2) of the levels of mercury in urine determined by direct determination and by standard addition method, compares quite favourably to that obtained by Coyle and Hartley (1981) who used the Magos reagent and CVAAS to determine mercury in urine and blood.

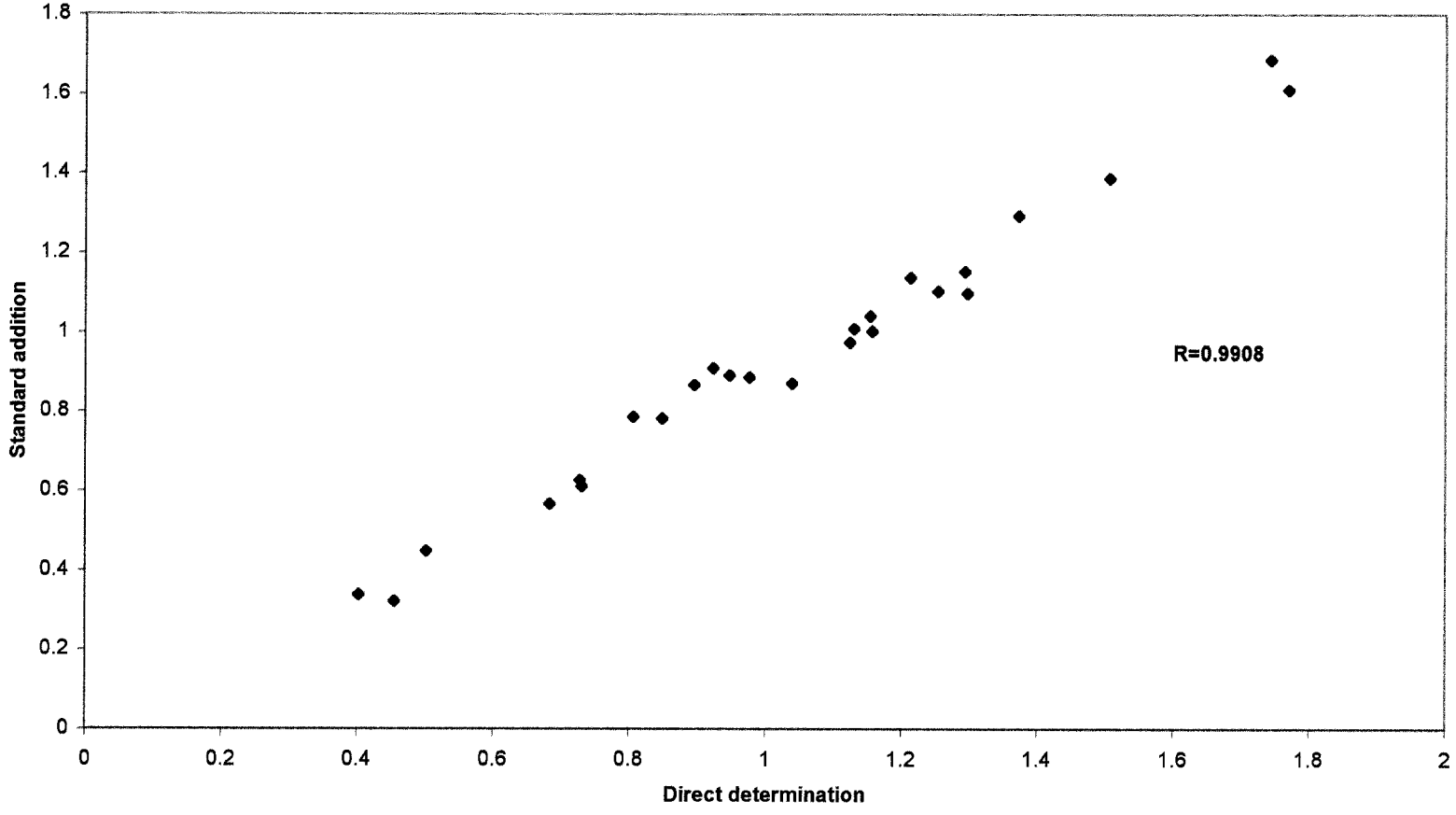

Figure 2. Scatter diagram of direct determination and standard addition of Hg in urine samples

Table 2. Summary of mercury levels in human blood, urine, hair, nail and fish tissues from different locations in the Ankobra and Tano river basins in South western Ghana

River Basin	Location	Blood/μgL^{-1} Mean± s (Range)	Urine/μgL^{-1} Mean± s (Range)	Hair/μgg^{-1} Mean± s (Range)	Nail/μgg^{-1} Mean±s (Range)	n	Fish tissues/μgg^{-1} (wet wt) Mean ± s (Range)	n
Ankobra	Anwiaso	102.0±55.8 (30.2–218)	34.2±36.0 (1.0–183)	1.61 ± 1.33 (0.15–5.86)	2.65±2.0 (0.57–10.0)	50	0.18± 0.1 (0.03-0.29)	7
	Sahuma	13.4±15.3 (2.1–68.1)	2.6 ±1.9 (0.13–6.96)	0.62 ± 0.41 (0.32–2.19)	0.73±0.91 (0.18–5.40)	50	0.32±0.6 (0.01-2.40)	21
Tano	Tanoso	16.5±10.7 (2.1–57.2)	6.4 ±2.7 (2.0 –14.3)	4.27 ± 6.26 (0.06–28.3)	3.45±4.16 (0.13–22.9)	51	0.20±0.1 (0.09-0.39)	11
	Elubo	39.5±16.2 (1.8–70.4)	7.3±6.9 (0.02–42.5)	1.21 ± 0.65 (0.07–3.19)	1.05±1.30 (0.22–9.68)	66	0.32±0.6 (0.05-2.50)	15

The overall results for the 217 subjects who gave blood, urine, hair and nail samples are summarised in Table 2. The mean blood and urine Hg concentrations for the 50 subjects of Anwiaso in the Ankobra river basin were significantly higher than those of the other groups. None of the Anwiaso subjects blood Hg concentration was less than 3 μg/L, the limit for non exposed persons; 24% of the subjects had blood Hg levels in the 3- 50 μg/L range, with 68% in the range of 50 – 200 μg/L and 8% above the 200 μg/L. The WHO (1980) urine Hg level at which industrial workers are recommended to be removed from further exposure, 50μg/L, was exceeded by 26% of the Anwiaso subjects. It may be possible that these subjects may have been exposed to some inorganic Hg vapour as a result of the 'galamsey' operations which involves amalgamation of the gold concentrate and later heating the amalgam to vaporise the Hg. The high blood Hg levels may not be unconnected with the heavy consumption of organic Hg in fish. The 51 subjects of Tanoso registered the highest mean levels of Hg in hair and nail with values of 4.27 μg/g and 2.65 μg/g respectively. Regression analysis of the data shows that the level of Hg in any matrix does not correlate linearly with age. It is of interest to note that the subject with the highest blood Hg of 218 μg/L is a 14 year old boy who incidentally, also registered the following Hg levels urine (67 μg/L), hair (3.08 μg/g) and nail (6.18 μg/g).

The level of Hg in the fish samples range from 0.01 – 2.50 μg/g wet weight. Concentrations of Hg generally increased with increasing length, weight and age of fish. This pattern, likely reflects bio-concentration of Hg along the food chain (Schofield et al. 1994)). Five fish samples (9.3%) exceeded 0.5ppm, the WHO (1976) standard for Hg level in fish, with seven other samples (13.0%) exceeding 0.3ppm, the EC Environmental Quality standard for a basket fish (MAFF 1987). Birke et al. (1972) who investigated the effects of ingestion of methyl mercury in contaminated fish, in Sweden, reported that no symptoms and signs of poisoning were observed in subjects consuming less than 0.8mg Hg as methyl mercury per day. In order to exceed this intake at the threshold concentration of 1.0ppm Hg, an individual would have to consume over 800g fresh fish per day. With the heavy fish eating habits of Ghanaians, the possibility of alarming clinical levels of Hg in blood may not be unlikely.

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